Study 191: Monitoring for Herbicide Residues in Plants of Interest to the Tribal People in Their Aboriginal Territory of Northwestern California

Protocol

Pamela L. Wofford

January 2000
Revised July 2001

Department of Pesticide Regulation
California Environmental Protection Agency
Environmental Monitoring and Pest Management
1001 I Street
Sacramento, California 95814

Department of Pesticide Regulation
Environmental Monitoring and Pest Management
830 K Street
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PROTOCOL

Study 191: Monitoring for Herbicide Residues in Plant of Interest to the Tribal People in Their Aboriginal Territory of Northwestern California

APPROVALS

Annie Yates — 7/9/01 (Date)
Sponsor (U.S. EPA)

John Sanders — 6/1/00 (Date)
Management (Dept. Pesticide Regulation)

Kean Goh — 1-28-00 (Date)
Management (Dept. Pesticide Regulation)

Pamela Wofford — 1-27-00 (Date)
Study Director (Dept. Pesticide Regulation)

Richard Currie — 4-03-00 (Date)
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Carissa Ganapathy — 5/29/01 (Date)
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Study xxx: Monitoring for Herbicide Residues in Plants of Interest to the Tribal People in Their Aboriginal Territory of Northwestern California

APPROVALS

Glenn E. Anderson — 2-8-2000
Glenn Anderson — Date
Del Norte County Agricultural Commissioner

John E Falkenstrom — March 15, 2000
John Falkenstrom — Date
Humboldt County Agricultural Commissioner

Leaf Hillman — 2-14-00
Leaf Hillman — Date
Karuk Tribe of California

for Kevin McKernan Pliny McCovey Jr. — 2-7-00
Kevin McKernan — Date
Hoopa Valley Tribal Council

Renee Stauffer — 2-7-00
Renee Stauffer — Date
Karuk Tribe of California

Ora Smith — 2/9/2000
Ora Smith — Date
Yurok Tribe of California

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Study 191: Monitoring for Herbicide Residues in Plants of Interest to the Tribal People in Their Aboriginal Territory of Northwestern California

January 2000
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I. INTRODUCTION

The use of native plant materials is a tradition among California Indian tribes. Tribal people use many different plants for food, basketry, medicine, and other cultural activities. Plants are integral to many facets of Indian culture and are gathered and handled in the ways of tribal tradition. Food and material resources are gathered throughout the year, using sites and techniques that are passed down in the family. The tribal people hold their plants in high reverence and are determined to protect their cultural resources and traditions.

There is a wide cross-section of plants that are gathered and represented in categories: berry or fruit plant, acorn or nut bearing plant, mushroom, perennial grass, fern, riparian shrub, and woody shrub. When gathered, these materials are collected in a variety of ways, depending on the plant species. Typically, each plant has a desirable part, whether it is roots, bark, foliage or stems, and only what is needed is taken. Basketweavers and gatherers collect forest materials often with their bare hands, and some materials are placed in the mouth and chewed to prepare them for weaving. The gathering sites may be near areas that herbicide may have been applied.

The timber industry uses "Best Management Practices", which may include the use of herbicides to control the growth of competitive vegetation prior to planting, during site preparation and for stand improvement. Some of the vegetation is important to the tribal people, and they are concerned about their potential exposure to forestry herbicides in gathering and use of these plant materials. For this reason, the tribal people of northwestern California have requested that the California Department of Pesticide Regulation (DPR) and the U.S. Environmental Protection Agency (EPA) monitor plants of interest for herbicide residues used in reforestation practices in that region.

II. OBJECTIVE

The objective of the project is to determine the presence of herbicide residues, frequency of occurrence and concentration in plants of interest to California tribes. If the results of this study indicate that unsafe residue levels are present in vegetation, and that the tribe are potentially being exposed to these levels, then further investigation may be warranted and mitigation measures proposed. Further actions will be taken if the offsite concentrations of herbicide residues exceed the US EPA reference dose RfD for 2,4-D and triclopyr of 0.01 mg/kg/day and 0.025 mg/kg/day, respectively (US EPA 1995). The calculation will include dermal, oral and food exposure. Actions could include mitigation measures of more restrictive application conditions, requiring further drift control, large buffer zones, etc.

III. SPONSOR

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Office of Pesticide Program
75 Hawthorne Street
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IV. COLLABORATORS

Susan Burdick, Ken Childs, Sr., Ron Johnson, Kevin McKernan, Jene McCovey, Lori Harder, Richard Myers, John Melvin, Marty Geslak
The Yurok Tribe
1034 Sixth Street
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Hoopa Valley Tribal Council
P.O.Box 1348
Hoopa, CA 95546

Lloyd Tangen, Bernie Bush, John Pricer
Simpson Timber Company
P.O. Box 245
Orick, CA 95555

V. TESTING FACILITIES AND PERSONNEL

The testing facilities are located at:

Department of Pesticide Regulation
Environmental Hazards Assessment Program
830 K Street
Sacramento, California 95814-3510

Department of Pesticide Regulation
Environmental Hazards Assessment Program
3971 Commerce Drive, Suite D
West Sacramento, California 95691

California Department of Food and Agriculture
Center for Analytical Chemistry
3292 Meadowview Road
Sacramento, California 95832

This cooperative sampling effort will be conducted by DPR's Environmental Hazards Assessment Program (EHAP) and Worker Health & Safety Branch staff, tribal representatives, U.S. EPA, and the County Agricultural Commissioners' staff, under the general direction of Kean S. Goh Ph.D., Program Supervisor.

Key personnel are listed below:

Project Leader:	Pam Wofford
Field Coordinator:	
Statistician:	Terri Barry, Ph.D.
Quality Assurance/Lab Liaison	Carissa Ganapathy
Chemist:	Catherine Cooper
Contact Person:	Kean S. Goh, Ph.D.

Responsibilities of the key personnel are described in EHAP Standard Operating Procedure ADMN002.00 (Supplement 1).

Questions concerning this monitoring study should be directed to Kean S. Goh at (916) 324-4100; fax, (916) 324-4088; e-mail, at <kgoh@cdpr.ca.gov>.

VI. EXPERIMENTAL DESIGN/STUDY PLAN

The dissipation and offsite movement of herbicide will be monitored. Selected plant type will be flagged and monitored every four months until nondetactable to determine dissipation of chemical. Offsite movement of herbicide will be monitored on selected

plants downwind from application and with measured distances from edge of spray area. Upon receipt of the spray plan, individual plant sites to be sampled will be selected, flagged, and documented using a global positioning system prior to the application. Plant sampling will begin immediately after major applications when plants of interest are available. Only aerial application of triclopyr will be monitored. Maximum number of samples should not exceed 100.

A. Vegetation

Tribal representatives will select a maximum of nine plants or plant parts of interest. These plants may include three broad categories: 1) basketry plants: willow sticks and roots, hazel sticks, maidenhair fern, Oregon grape's roots and stems; 2) food plant: tan oak acorns, huckleberry; 3) medicinal plants: yarrow, etc.

B. Herbicide

Triclopyr is applied by helicopter and has the highest potential for drift. Triclopyr will be analyzed for dislodgeable residue on basketry materials and total residue in food and medicinal plants. Date, total amount applied, acreage applied and application method and climatic condition during application will be recorded and precipitation recorded during the duration of the study.

C. Sites

Plant samples will be taken within a sprayed area, near a sprayed area, and in traditional tribal gathering sites within the Karuk, Hupa, and Yurok aboriginal territories. More samples will be allocated to sprayed areas and areas adjacent to applications. Samples will be taken from within the treatment area and outside the treatment area.

VII. SAMPLING METHODS, SAMPLE STORAGE, SAMPLE TRANSPORT, AND CHEMICAL ANALYTICAL METHODS

A. Vegetation and Environmental Sampling Methods

The method for collecting plant samples for total residue analysis is described in EHAP Standard Operating Procedure FSOT001.01 (Supplement 2). All samples will be frozen from the time of collection until laboratory analysis.

All sampling information and analytical results will be recorded on the chain of custody form as described in EHAP Standard Operating Procedure ADMN006.00 (Supplement 3). Preparation of sample containers will follow procedure listed in EHAP Standard Operating Procedure QAQC005.00 (Supplement 4).

B. Analytical Methods

Analytical methods have been developed for some of the plant species. The analytical methods for total residues will be validated, and the standard operating procedures

written and approved concurrently with sampling, but prior to laboratory analysis of the samples (Supplement 5).

C. Quality Assurance/Quality Control

This study will comply with U.S. EPA requirements for Good Laboratory Practices (40 CFR, Part 160).

Method Detection Limits were determined according to EHAP Standard Operating Procedure QAQC001.00 (Supplement 6) and U.S. EPA procedure (40 CFR, Part 136, Appendix B). The Method Detection Limit for each chemical and plant will be given in the analytical Standard Operating Procedure.

Method validation for the triclopyr to be used in vegetation monitoring follows EHAP Standard Operating Procedure QAQC001.00. The spike levels are chosen based on the range of concentrations anticipated in vegetation. The mean recovery and standard deviation are calculated for each compound. Warning limits are established at the mean recovery plus/minus two times the standard deviation. Control limits are established at the mean recovery plus/minus three times the standard deviation.

Laboratory continuing quality control will follow EHAP Standard Operating Procedure QAQC001.00 and include the following:

Matrix blank: 1 sample per extraction set
Matrix spike: 2 sample per extraction set

Any spike samples falling outside the warning or control limits will have the appropriate corrective steps taken as described in EHAP Standard Operating Procedure QAQC001.00.

D. Sample Storage, Transport and Tracking

All vegetation samples will be stored on dry ice and maintained at -10^{0}C as described in EHAP Standard Operating Procedure QAQC004.01 (Supplement 7) until chemically extracted. Sample tracking is described in EHAP Standard Operating Procedure QAQC003.01 (Supplement 8).

VIII. DATA ANALYSIS

Results will be reported as parts per million (ppm) fresh weight basis for total residue. Descriptive statistics will be used to characterize vegetation data.

IX. ESTIMATED TIMETABLE AND NUMBER OF SAMPLES

Sampling is expected to occur through the 2000-2001 study year, and subsequently, intermittent progress reports will be issued to interested parties prior to completion of the

final report.

Chemical Analytical Method Development: January 2000
Sampling Period: March 2000-March 2001
Chemical Analyses: March 2000
Status Progress Report: quarterly
Final Report: May 2001

Number of samples: 40 dissipation, **50** off-site, **10** QC =100

X. RECORDS TO BE MAINTAINED

The following documents will be maintained at the testing facility as described in SOP ADMN005.00 (Supplement 9).

1. All raw data other than those records maintained by the laboratory.
2. The study protocol bearing the original signatures of the study director, sponsor, and quality assurance officers, including amendments and documentation of deviations.
3. All correspondence necessary to reconstruct the study.
4. All progress reports and audits.
5. Documentation of the training and experience of personnel involved in the study.
6. A copy of the final report.

XI. REFERENCES

Middendorf, Paul J. Forest worker exposures to triclopyr (3,5,6-trichloro-2-pyridinyloxyaceticacid), butoxyethyl ester during directed foliar applications of Garlon4 herbicide. Registrant study submitted by DowElanco. Produced by United States Department of Agriculture Forest Service Federal Identifier #08-89-53-01 Project # A-8416-000.

Spencer, Janet. 1998. Exposure of Mixer/Loader/Applicators to Triclopyr in Forest Settings. California Dept. of Pesticide Regulation. Worker Health and Safety (WH&S) Project Number: 9501.

U.S. Environmental Protection Agency. Integrated Risk Information System Database, Washington, DC, 1995.10-14

SUPPLEMENT 1
EHAP Standard Operating Procedure ADMN002.00
Personnel Organization and Responsibilities for Studies

California Department of Pesticide Regulation
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STANDARD OPERATING PROCEDURE
Personnel Organization and Responsibilities for Studies

KEY WORDS

management; project supervisor; project leader; senior scientist; field coordinator; quality assurance officer; laboratory liaison; statistician; chemist; contact person; GLP; safety; problem resolution

APPROVALS

APPROVED BY: John L. Sanders DATE: 3/6/97
Management

APPROVED BY: K L Z DATE: 3-5-97
EHAP Senior Scientist

APPROVED BY: Randy Segawa DATE: 2-26-97
EHAP Quality Assurance Officer

PREPARED BY: Randy Segawa DATE: 2-26-97

No previous SOP exists; however, this SOP does supersede the following policy memos:

Goh, K.S. Responsibilities of Field Coordinator for EHAP studies. Memorandum to EHAP Personnel, dated 9/24/93.

Sanders, J. Responsibilities of Project Leaders Regarding Chemical Analysis. Memorandum to EHAP Staff, dated 6/13/88.

Sanders, J. Lab Liaison Personnel and Policy. Memorandum to EHAP Personnel, dated 7/1/87.

STANDARD OPERATING PROCEDURE
Personnel Organization and Responsibilities for Studies

1.0 INTRODUCTION

1.1 Purpose

This Standard Operating Procedure (SOP) defines and discusses the organization and responsibilities of personnel for Environmental Hazards Assessment Program (EHAP) studies. This SOP primarily applies to EHAP field studies, but can also apply to non-field projects.

1.2 Definitions

1.2.1 **Branch** refers to an organizational unit within the Department of Pesticide Regulation (DPR). There are six branches within DPR as shown in Figure 1.

1.2.2 **Protocol** refers to a written document that describes the objectives, personnel, study design, sampling procedures, analytical procedures, data analysis, and schedule for a specific study.

1.3 EHAP Organization

The EHAP is a unit within the Department of Pesticide Regulation (DPR) and provides technical support and monitoring regarding the environmental fate of pesticides. The department and organization of program personnel are shown in Figure 1.

2.0 STUDY ORGANIZATION

Figure 1 shows that the EHAP is organized into groups by function or technical specialty. Personnel are organized into a team for each study. Key study personnel include the Management, Project Supervisor, Project Leader, Senior Scientist, Field Coordinator, Laboratory Liaison, Quality Assurance Officer, Statistician, Chemist and Contact Person. The personnel listed above may not be included in all studies. With certain restrictions, the duties of two or more people may be performed by one person (e.g., the duties of the Project Supervisor and Project Leader may be performed by a single person). The most common personnel organization for a study is shown in Figure 2. The Project Supervisor is selected by the branch chief and/or program supervisor. The Project Leader and other team members are selected by the program supervisor and group supervisors. Selection of all team members should be made

early in the developmental stages of a study to allow them time to understand what management wants to accomplish and to allow sufficient time to prepare for implementing the study.

3.0 PERSONNEL RESPONSIBILITIES

The following personnel have specific responsibilities when assigned to a study.

3.1 Management - Management typically consists of the Assistant Director and Branch Chief and sometimes the Program Supervisor. Management has responsibility for all policy issues, includng the following:

- 3.1.1 determines the objective of a study
- 3.1.2 selects the project supervisor
- 3.1.3 gives final approval for the study protocol, including the budget
- 3.1.4 gives final approval for all SOPs
- 3.1.5 gives approval to any changes in finalized protocols
- 3.1.6 sets study deadlines
- 3.1.7 gives final approval for the study report and any interim memos

3.2 Project Supervisor - The Project Supervisor is typically the supervisor of the Project Leader (i.e., a senior environmental research scientist (supervisor) or the Program Supervisor). The Project Supervisor has overall responsibility for the administrative and technical aspects of the study, including the following:

- 3.2.1 refines the study objectives
- 3.2.2 selects the Project Leader
- 3.2.3 gives general direction to the Project Leader
- 3.2.4 acts as editor-in-chief for review of documents (e.g. protocol, memos, SOPs, report)
- 3.2.5 reviews and approves any changes in finalized protocols
- 3.2.6 supervises administrative tasks (e.g., contracts, purchases, hires)
- 3.2.7 supplies personnel and resources to the Project Leader
- 3.2.8 establishes responsibilities of each team member - consulting with Project Leader
- 3.2.9 facilitates communication with other groups and other branches
- 3.2.10 responsible for safety - determines safety procedures and disseminates hazard communication information - consulting with other DPR branches
- 3.2.11 helps resolve scientific differences of opinion

If the study is conducted under Good Laboratory Practices (GLP), the Project Supervisor is assigned to Management and is also responsible for the following:

3.2.12 establishes a quality assurance unit
3.2.13 assures that test and control substances or mixtures have been tested for identity, strength, purity, stability and uniformity
3.2.14 assures that any deviations from GLP are communicated to the Study Director (Project Leader) and corrective actions are taken and documented

3.3 Project Leader - The Project Leader is typically an environmental research scientist (ERS), associate ERS, or a senior ERS. The Project Leader has primary responsibility for all technical aspects of a study, including the following duties. Some of the following responsibilities may be delegated to other team members.

3.3.1 gathers background information for study - conducts literature search, gathers pesticide use data
3.3.2 identifies personnel needs - sampling, chemical analysis, data analysis
3.3.3 formulates study plan after consulting with team members
3.3.4 writes and follows study protocol and any changes
3.3.5 coordinates protocol dissemination with contact person
3.3.6 communicates with study cooperators - growers, agencies
3.3.7 specifies lab goals through lab liaison - methodology, validation, reporting limits, quality control, turnaround time
3.3.8 interacts with interested parties through the contact person - agencies, public
3.3.9 develops chain of custody form - consults with team members
3.3.10 conducts administrative tasks - contracts, timesheets, purchases, services, budget, expenditures tracking
3.3.11 documents all study activities
3.3.12 obtains necessary permits
3.3.13 determines sampling methodology - consulting with team members
3.3.14 determines sampling schedule - consulting with field coordinator
3.3.15 prepares all pertinent SOPs
3.3.16 trains personnel in study tasks
3.3.17 supervises field sampling and/or data collection
3.3.18 arranges for special facilities - storage, experimental plots
3.3.19 determines sample priorities for lab analysis

3.3.20 reviews and accepts data from the lab
3.3.21 designates samples for reanalysis
3.3.22 reviews laboratory SOPs
3.3.23 supervises data analysis
3.3.24 writes interim progress reports or memos
3.3.25 writes final report - with other team members
3.3.26 coordinates report dissemination with contact person
3.3.27 archives study data
3.3.28 presents results to various audiences

If the study is conducted under GLP, the Project Leader is designated as the Study Director and is also responsible for the following:

3.3.29 corrective actions are taken and documented when necessary
3.3.30 GLP requirements are followed

3.4 Senior Scientist - The Senior Scientist is typically a senior ERS (specialist). The duties of the Senior Scientist and Project Leader cannot be performed by a single person. The Senior Scientist reviews and approves a study for scientific adequacy, including the following specific duties:

3.4.1 gives technical advice to the Project Leader
3.4.2 reviews and approves protocols, memos, SOPs (including lab SOPs) and reports for scientific adequacy
3.4.3 helps resolve scientific differences of opinion
3.4.4 reviews and approves revisions to protocols and SOPs
3.4.5 reviews and approves final report

If the study is conducted under GLP, the Senior Scientist is assigned to the Quality Assurance Unit and assists the Quality Assurance Officer.

3.5 Field Coordinator - The Field Coordinator is typically an associate ERS, ERS, or environmental research assistant from one of the field groups. The Field Coordinator oversees the collection of field samples and has responsibility for field safety. He/She may have more or fewer duties depending on the preference of the Project Supervisor and Project Leader. The Field Coordinator will normally act for the Project Leader in the Project Leader's absence. More than one Field Coordinator may be assigned for very complex studies. The Field Coordinator is normally responsible for the following duties:

3.5.1 decides safety issues under direction of Project Supervisor - the Field Coordinator has the authority to modify or terminate any field activity which threatens the health or safety of field personnel; provides or arranges for safety training
3.5.2 assembles sampling materials
3.5.3 purchases needed materials
3.5.4 arranges transportation and housing
3.5.5 checks and calibrates equipment
3.5.6 assists in developing chain of custody format
3.5.7 assists in coordinating activities with study cooperators
3.5.8 assists in selecting sampling sites
3.5.9 gives advice on sampling methodology
3.5.10 assists in the preparation of SOPs
3.5.11 recommends personnel needs and sampling schedule
3.5.12 prepares sampling materials list
3.5.13 collects and transports samples
3.5.14 coordinates sampling schedule with the Lab Liaison
3.5.15 cleans sampling materials
3.5.16 supervises field sampling in the absence of the Project Leader
3.5.17 assists in the protocol preparation
3.5.18 assists in the report preparation

3.6 Quality Assurance Officer - The Quality Assurance Officer is typically an associate ERS. Duties of the Quality Assurance Officer and Laboratory Liaison are typically performed by one person. The Quality Assurance Officer cannot perform the duties of the Project Leader or Field Coordinator. The Quality Assurance Officer is responsible for documentation and the quality of the laboratory analysis, including the following specific duties:

3.6.1 assists the Project Leader in specifying laboratory methodology
3.6.2 assists the Project Leader in specifying laboratory quality control procedures
3.6.3 reviews and approves EHAP SOPs
3.6.4 maintains copies of protocols and EHAP SOPs
3.6.5 reviews, compiles and disseminates quality control data
3.6.6 notifies Project Leader of analytical problems
3.6.7 initiates lab corrective actions - consulting with Project Leader
3.6.8 arranges the preparation of quality control samples

3.6.9 resolves lab discrepancies
3.6.10 produces method validation and quality control tables for the report
3.6.11 obtains and disseminates laboratory SOPs
3.6.12 reviews laboratory SOPs

If the study is conducted under GLP, the Quality Assurance Officer supervises the Quality Assurance Unit and is responsible for the following:

3.6.13 maintains master schedule of EHAP GLP studies
3.6.14 determines that all known deviations from the protocol or SOPs were authorized and documented
3.6.15 prepares and signs statement of dates of inspection and findings to be included in final report
3.6.16 reviews and approves protocol and final report

3.7 Laboratory Liaison - The Laboratory Liaison is typically an associate ERS. Duties of the Laboratory Liaison and Quality Assurance Officer are typically performed by one person. The Laboratory Liaison is responsible for coordinating activities between EHAP and the chemistry labs, including the following duties:

3.7.1 acts as liaison between the Project Leader and the labs
3.7.2 selects the chemistry laboratories (primary and quality control)
3.7.3 negotiates analytical specifications with the labs (described in SOP QAQC001)
3.7.4 stores and transports samples to the labs
3.7.5 controls timing and quantity of samples delivered to the lab
3.7.6 tracks movement of samples between storage facility and lab
3.7.7 transmits lab data to the Project Leader
3.7.8 administers lab contracts

3.8 Chemist - The Chemist typically works for the Department of Food and Agriculture or a commercial lab, not EHAP. The Chemist is responsible for the pesticide analysis of samples. He/she also gives advice on sampling methodology.

3.9 Statistician - The Statistician is typically an associate ERS. The Statistician is responsible for the design and statistical analysis of the study, including the following specific duties:

3.9.1 determines the study design - consulting with other team members
3.9.2 assists in writing the protocol

3.9.3 reviews and approves the study protocol and any changes
3.9.4 conducts statistical analysis of the study data
3.9.5 assists in writing the final report
3.9.6 reviews final report

3.10 Contact Person - The Contact Person is typically assigned from Program Representation of the Environmental Monitoring Branch. The Contact Person acts as liaison with the public, branches, and agencies that are interested but not participants in the study. His/Her specific duties include the following:

3.10.1 develops interested parties list - consulting with the Project Leader
3.10.2 acts as liaison to public/branches/agencies
3.10.3 disseminates appropriate documents to interested parties
3.10.4 coordinates review of documents with interested parties
3.10.5 assists the DPR communications office with media inquiries
3.10.6 writes executive summary
3.10.7 advises Project Leader on policy and regulatory issues of study

3.11 Other EHAP and DPR Personnel - Designated personnel provide support services. EHAP warehouse personnel provide storage, maintenance, equipment and transportation upon request. EHAP laboratory facilities are available for soil characterization and other analyses upon request. A number of people within and outside of EHAP provide special computer services such as programs, databases, modeling, geographic information systems, or graphics upon request. The Worker Health and Safety, and Medical Toxicology Branches can provide information on toxicity, safety precautions as well as medical monitoring upon request. These support personnel may not be available for all studies and should be requested through the Project Supervisor or the appropriate Group Supervisor.

4.0 PROBLEM RESOLUTION

Technical items that are not specified here are the responsibility of the Project Leader. Both the Project Leader and Senior Scientist should agree on all technical issues. The Project Supervisor is responsible for resolving any disagreements. Administrative, policy or other items not specified here are the responsibility of the Project Supervisor.

5.0 SAFETY

Personnel safety is of primary importance at all times. The Project Supervisor and Field Coordinator have primary responsibility for safety. However, all team members must follow correct safety procedures. Approval for changing the protocol or a SOP should be sought whenever possible, but may not be possible if an imminent danger exists. A study should always be conducted in a safe manner, no matter what the protocol or SOP specifies. Document all changes in the protocol or SOP.

In the absence of the Field Coordinator, the ranking field group person has primary responsibility for safety while working in the field.

6.0 STUDY-SPECIFIC DECISIONS

Management, Project Supervisor and Project Leader are responsible for the following study-specific decisions:

6.1 Selection of study personnel
6.2 Responsibilities of each team member

7.0 REFERENCES

Goh, K.S. Responsibilities of Field Coordinator for EHAP studies. Memorandum to EHAP Personnel, dated 9/24/93.

Sanders, J. Responsibilities of Project Leaders Regarding Chemical Analysis. Memorandum to EHAP Staff, dated 6/13/88.

Sanders, J. Lab Liaison Personnel and Policy. Memorandum to EHAP Personnel, dated 7/1/87.

APPENDICES

Figure 1. Department of Pesticide Regulation Personnel Organization

Figure 2. EHAP Study Personnel Organization

Figure 1

Department of Pesticide Regulation Personnel Organization

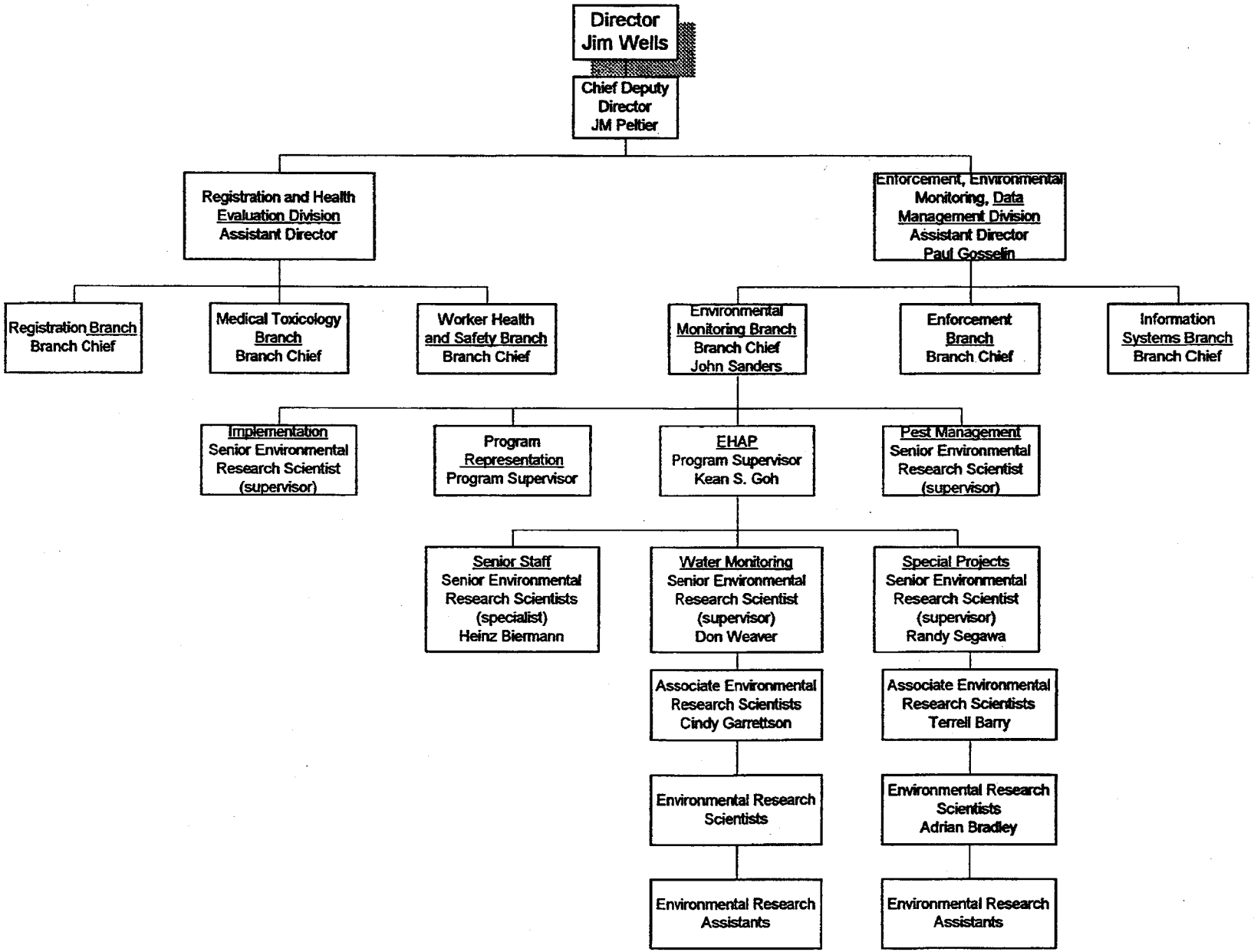
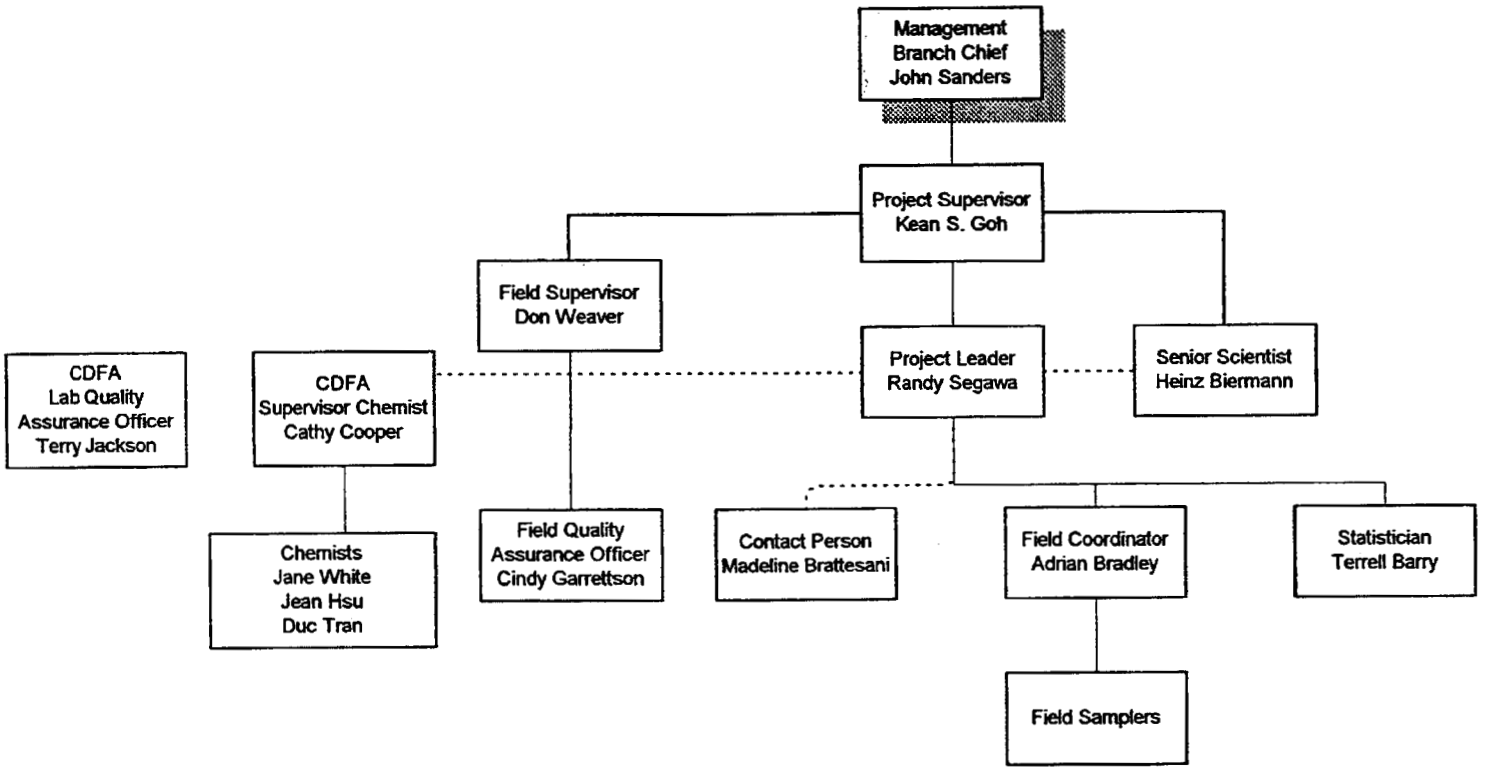


Figure 2

EHAP Study Personnel Organization*



*For GLP studies, the Senior Scientist and Quality Assurance Officer make up the Quality Assurance Unit and report to Management

SUPPLEMENT 2
EHAP Standard Operating Procedure FSOT001.01
Sampling Plants of Interest to Native Americans

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
1020 N Street
Sacramento, California 95814

STANDARD OPERATING PROCEDURE

Sampling Plants of Interest to Native Americans

KEY WORDS
vegetation, basketweaver

APPROVALS

APPROVED BY: _____ DATE: 4-3-98
Management

APPROVED BY: _____ DATE: 3-30-98
EHAP Senior Scientist

APPROVED BY: _____ DATE: 4/2/98
EHAP Quality Assurance Officer

PREPARED BY: Randy Segawa DATE: 3-26-98

Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE

Sampling Plants of Interest to Native Americans

1.0 INTRODUCTION

1.1 Purpose

This Standard Operating Procedure (SOP) discusses procedures for sampling vegetation used by Native American basketweavers. Refer to the study protocol for information regarding plant type selected, plant parts that are sampled, and storage procedures. The study protocol specifies the manner in which vegetation is selected for sampling but not the procedure for collecting a vegetation sample. Therefore, this SOP describes the method of collecting a vegetation sample for subsequent analysis.

2.0 MATERIALS

disposable gloves
glass jars
collection tool (shovel, trowel, clippers, forceps, scissors)
storage unit and coolant (ice chest with dry or wet ice)
balance
chain of custody
pen
clipboard
alcohol
deionized water
Liqui-Nox® liquid cleaning soap
2 hand-held nylon bristle brushes (optional)
Plastic bags (4 inch x 8 inch or larger) - to hold clippers and trowels
Several plastic garbage bags (13-gallon size)
Several cleaning sponges or abrasive scrubbing pads

3.0 PROCEDURES

3.1 General

Vegetation sampling in this study is conducted for the purpose of determining the internal residue of a pesticide.

3.2 Sampling Methods

3.2.1 *Sampling foliage.* Locate the appropriate species within the designated sampling area (inside or outside treatment area). Wearing disposable gloves, use a pre-cleaned cutting tool (scissors, clippers) to cut small amounts of vegetation from the entire plant. Make sure to include foliage from all parts of the canopy: top, bottom, inside, outside, etc. While cutting, hold the glass jar so that foliage falls directly into it. Avoid handling foliage prior to including it in the sample.

3.2.2 *Sampling roots.* Locate the appropriate species within the designated sampling area (inside or outside the treatment area). Using a clean shovel or trowel (depending on digging difficulty), dig a hole around the plant to loosen the roots. Avoid cutting or otherwise breaking roots. Once a sufficient amount of material can be loosened from the soil, prepare to collect the sample. Put on disposable gloves, open the glass jar, shake off excess soil, and place roots in the jar. Use clippers or scissors to cut above-ground foliage from roots. Push disturbed soil back into the hole, bury any excess roots that were dug up but not included in the sample, and otherwise make every effort to return the area back to its original condition.

3.2.3 *Sampling brush.* Locate the appropriate species within the designated sampling area (inside or outside the treatment area). Wearing disposable gloves, use a pre-cleaned cutting tool (scissors, clippers) to cut small amounts of vegetation from the entire plant. Include only new growth (shoots) in the sample, avoiding old (woody) parts. Outer leaves may need to be cut from shoots depending on species (willow, deerbrush).

3.2.4 *Sampling berries.* Locate the appropriate species within the designated sampling area (inside or outside the treatment area). Wearing disposable gloves, pick berries from the entire plant: top, bottom, inside, and outside. Hold collection container (glass jar) up to the plant while collecting, so that berries fall directly into the jar. As much as possible, avoid handling the berries.

3.3. Weighing Samples.

Before collecting a sample, weigh and record the weight (in grams) of each jar used for collection. Do not include the cap in the measurement. Record the weight in the appropriate space provided on the chain of custody (see below). After collecting the sample, record the weight in the appropriate space provided on the chain of custody. Do

not include the cap in the measurement. Cover the top of the jar with an aluminum foil sheet and screw the cap on tightly. Store samples according to SOP QAQC004 immediately.

3.4. Cleaning Sampling Equipment

This general procedure should be followed for clean or unclean hand clippers. It is always important that the clippers which are designated for use in the pesticide treated areas (**dissipation locations**) be **isolated** from the clippers which are designated for use in the untreated areas (**off-site locations**). Failure to follow these guidelines may result in inadvertant pesticide contamination of plant material samples.

Separately wash the dissipation and off-site location hand clippers in different, *shallow* plastic containers. Each container should be lined with a clean, 13-gallon plastic garbage bag which will contain the cleaning solution.

To each container, add an adequate amount of de-ioinzed water and Liqui-Nox cleaning soap. Using a clean sponge or abrasive scrubbing pad, vigorously scour the clipper cutting blades to remove all plant residue which may have built up on the cutting surface. Also thoroughly clean the remaining portion of the hand clippers. Rinse copiously with de-ionized water and then with isopropyl alcohol. Let the clippers air dry.

After the sampling equipment is clean and dry, place hand clippers in a clean plastic bag, remembering to isolate the dissipation and off-site clippers into different sampling boxes. Discard the de-ionized wash water, plastic bag, cleaning sponges, and abrasive scrubbing pads. Prepare a new wash solution(s) at each sampling site and follow procedure above.

The general cleaning procedure for hand trowels and shovels is the same as above, although these sampling materials are not separated into dissipation or off-site equipment. After each use all sampling equipment should be cleaned. Always inspect equipment prior to use and clean it if it appears dirty. Cleaned equipment should be stored in plastic bags to avoid contamination.

Using deionized water and a nylon brush, loosen dirt and plant material from the collection tool. Avoid the sharp edges of clippers, scissors, etc. by using the brush, holding the tool by the handle. Rinse with deionized water and repeat as needed. When the collection tool appears clean, rinse three more times with deionized water. Using a squeeze bottle

filled with isopropyl alcohol, rinse equipment and store it in a plastic bag.

4.0. REPORTING REQUIREMENTS

4.1 Chain of Custody

A chain of custody form should be completed for each sample according to SOP ADMN006. The following information should be recorded on the chain of custody:

4.1.1 *Study number*
4.1.2 *Sample number*
4.1.3 *Sample location*
4.1.4 *Date and time of sampling*
4.1.5 *Sampling personnel*
4.1.6 *Name of field or experimental plot*
4.1.7 *Plant species and part*

4.2 Ancillary Information

Additional information should be recorded or included in the experimental notebook, including a map of the sampling location(s), weather conditions, time elapsed after application, general condition of plants.

5.0 STUDY-SPECIFIC DECISIONS

The following study specific decisions are the responsibility of the study project leader, and should be made in consultation with the study field coordinator, senior scientists, and EHAP Quality Assurance Officer.

5.0.1 *Sampling location*
5.0.2 *Sampling method*
5.0.3 *Sample storage*
5.0.4 *Sampling duration*

REFERENCES

Ganapathy, C. 1996. Creating and filling out a chain of custody record. SOP ADMN006.00.

Nordmark, C. 1996. Procedure for packaging and transporting samples. SOP QAQC004.00.

SUPPLEMENT 3
EHAP Standard Operating Procedure ADMN006.00
Creating and Filling out a Chain of Custody Record

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
1020 N Street
Sacramento, California 95814

STANDARD OPERATING PROCEDURE
Creating and Filling out a Chain of Custody Record

KEY WORDS

COC, Sample Tracking

APPROVALS

APPROVED BY: John L. Sanders DATE: 3/6/97
Management

APPROVED BY: H. L. B DATE: 2-27-97
EHAP Senior Scientist

APPROVED BY: Randy Segawa DATE: 2-26-97
EHAP Quality Assurance Officer

PREPARED BY: C. Gana DATE: 2-26-97

Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE
Creating and Filling out a Chain of Custody Record

I.0 INTRODUCTION

1.1 Purpose

A chain of custody record (COC) is an appropriate format to record important data associated with each individual sample. Normally, a COC is used to record three types of information; field information, laboratory information, and the people who handle the sample. This SOP discusses procedures for the third item, handling the sample. The other two items are discussed in other SOPs.

1.2 Definitions

Chain of Custody (COC) is a legal document designed to track persons who are responsible for the preparation of the sample container, sample collection, sample delivery, storage, and sample analysis.

A **sample number** is a unique number given to a sample, usually attached to the sample container with label tape (SOP QAQC005.00).

2.0 PROCEDURES

2.1 Creating the COC

A specific COC is created for each study. A COC normally has three sections: field information, lab information, and the signatures of the people who handle the sample. The form is generally a three-page carbon copy document, including a white, yellow and pink sheet.

2.1.1 Field Information - The COC must contain places to enter the following field information: study number, sample number, sampling date, and type of sample. Other field information may be recorded **as** specified in the study protocol.

2.1.2 Laboratory Information - The COC must contain places to enter the following laboratory information: reporting limit of each analyte, the result of analysis, date of extraction, date of analysis, and the signature of the person performing extraction and analysis. Other laboratory information may be recorded

as specified in the study protocol.

2.1.3 Signatures - The COC must contain places for all people who handle the sample to sign his/her name. This is a record of persons who had custody of the sample during all steps of the process from container preparation, sample collection, sample storage and transport, and sample analysis. There should be signature lines to relinquish custody of the sample and to receive custody of the sample.

2.2 Filling out the chain of custody

The first "relinquished by" line is normally signed by the person who prepared the sample container. The "received by" line is normally signed and dated by the person collecting the sample, that person then signs to relinquish the sample. The person who transports the sample to the laboratory signs last. In case there are additional steps in the process requiring another person or persons to take custody of the sample, the form has additional lines for signatures. The line at the bottom of the page is provided for personnel from the laboratory to sign for receiving the sample.

No erroneous information may be erased on the COC. Errors must be lined out and initialed, and the correction written in. Furthermore, a COC may not be destroyed or discarded and must be retained by the project leader.

2.2.1 Container Preparation - The COC should be initiated at the time the containers are prepared (SOP QAQC005.00). The COC at that time should include the study number, the sample number (which should correspond with a unique number on a sample container), chemicals to be analyzed if known, and the signature of the person preparing the sample container and date prepared.

2.2.2 Sample Collection - The personnel who receive the sample containers, transport them to the field, collect the samples, and place them in containers normally sign their name on the COC under the first received by column and write the date and time the sample container was received on the line next to it. They also fill in the information required on the COC and sign the relinquished by line.

2.2.3 Sample Storage - When the samples are relinquished to the EHAP sample custodian, that person will sign the COC on the next "received by" line, and will write the date and time. The pink copy of the COC is detached from the other two

copies. Pink COC sheets are be retained at the sample storage facility until they are entered into the sample tracking database (SOP QAQC 003), at which point they should be given to the project leader.

2.2.4. Sample Delivery - Once the sample is delivered to the lab, the laboratory personnel will sign and date the "received by" line located at the bottom of the COC.

2.2.5. Laboratory Analysis - The analyzing laboratory will record the reporting limit of each analyte, the result of analysis, date of extraction, date of analysis, and the signature of the person performing extraction and analysis. When the analysis is completed and approved by the laboratory, white COC sheets will be given to the sample custodian. The yellow copy is retained by the laboratory.

2.2.6 Data Review and COC Delivery - The appropriate information is entered into the sample tracking database. If a quality assurance officer is assigned to the study, they will review the analytical data. The white COC is then forwarded the project leader.

SUPPLEMENT 4
EHAP Standard Operating Procedure QAQC005.00
Preparation of Sample Containers

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
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STANDARD OPERATING PROCEDURE
PREPARATION OF SAMPLE CONTAINERS

KEY WORDS

Six-pack, Sample-Pack; Storage-Pack; Bottle preparation; VOA; COC;

APPROVALS

APPROVED BY: _____ DATE: 12/18/98
Management

APPROVED BY: _____ DATE: 12/8/98
EHAP Senior Scientist

APPROVED BY: _____ DATE: 12/14/98
EHAP Quality Assurance Officer

PREPARED BY: _____ DATE: 12/15/98

Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE
PREPARATION OF SAMPLE CONTAINERS

1 .O INTRODUCTION

1 .I Purpose

This Standard Operating Procedure (SOP) discusses preparing, labeling and packaging containers to be used for collecting water or soil samples. This SOP will describe two commonly used methods for packaging sample containers by the Environmental Hazards Assessment Program as well as Chain of Custody (COC) handling. Study specific decisions may be made by the project leader regarding sample container preparation and may be described in the study protocol.

1.2 Definitions

1.2.1 A **sample container** holds the medium being sampled, e.g. soil, water, air, plant material, etc. when analyzed for pesticides. Containers are typically made of glass to prevent pesticide adsorption to the container. Some pesticides will adsorb to glass so check with the analytical chemist. Typically, soil is collected in pint or quart mason jars, water in amber bottles, air in charcoal tubes or vials, and plants in mason jars. Note: some chemicals degrade in sunlight so if glass containers are not tinted, care should be taken to transport and store samples in the dark.

1.2.2 A **Chain of Custody (COC)** is a legal document designed to track a sample container from container preparation through sample analysis as defined in SOP ADMN006.00.

1.2.3 A **Sample-Pack** is polystyrene "six-pack" or plastic bag that houses a set of sample containers. The sample-pack is intended to hold samples from a single site, representing a single sampling event such as sampling one ground water well. Each container within the sample pack has a sample number.

1.2.4 A **Storage-Pack** is a box of sample containers designated for a single study. The storage-pack is usually kept in the manufacturer's original shipping box. Each container in a storage-pack has a sample number;

however, the containers are not intended for a single sampling site like sample-packs. The storage-pack or packs are frequently used to store sampling containers in the warehouse and used as needed for a given study.

2.0 MATERIALS

2.1 New or cleaned sample containers as detailed in the study protocol.
2.2 Labels pre-printed with Study Number, Sample Number, and Sample Type.
2.3 Clear adhesive tape wide enough to cover a label.
2.4 COCs appropriate to the study.
2.5 For bottles to be packaged as sample packs:
- (a) Polystyrene "six-pack" bottle trays.
- (b) Large (minimum 24 X24 inches) plastic bags.
- (c) Small (minimum 6 X 12 inches) plastic bags.
- (d) Rubber bands.

2.6 For bottles to be packaged as storage packs:
- (a) Shipping box for appropriate sample containers, normally a 12-pack.
- (b) Self-adhesive labels (approximately 2 X 3 inches)

2.7 For Volatile Organic Analysis (VOA) sample vials:
- (a) Medium resealable plastic bags (minimum 6 X10 inches).
- (b) Large resealable plastic bags (minimum 12 X 16 inches).
- (c) Cardboard file box.

2.8 Permanent marking pen.

3.0 PROCEDURES

3.1 Sample Container Preparation

3.1 .I Obtain sufficient sample containers, labels, COCs and other supplies to complete the required number of sample containers/packs required by the study. Ensure that the containers are of the proper type and size for the sampling medium as well as the analytical lab's requirements. Labels

need to be printed with the study number, unique sample number, and sample type (e.g., water, soil, etc.) for every container that will be used. A spread-sheet program works well for making labels.

3.1.2 Remove sample containers from the shipping box (storage-pack) and check their condition. Ensure the cap is secure and the containers are clean and undamaged. Discard any bottles that have lost their caps during transport or are damaged. Wipe off any accumulated dust.

3.1.3 Cut out a pre-printed label and affix it horizontally to the sample container using the clear tape. Labels must be placed high enough on the sample containers that they will not be submerged by water accumulating in the individual wells of the six-pack or ice chest. Smooth the tape to assure a good seal around the label.

3.1.4 Place the sample container in a sample-pack or back in the storage-pack as required, as detailed below in 3.4 and 3.5. The exception is Volatile Organic Analysis (VOA) vials.

3.1.5 For VOA vials, follow the individual study protocol for the number of bottles per sample and whether to make sample- or storage-packs. VOA vials are normally packaged as three vials bearing the same sample number (replicates). These vials are placed together in a resealable plastic bag and treated as a single sample. Using a permanent marker, label each individual bag of 3 vials as primary (P) for the lowest sample number, (Bl , B2, etc.) for the backups, through field blank (FB) for the highest sample number. Check with the project leader, since he or she may number and name replicates as they choose. The individual packages are then combined in a larger resealable plastic bag to form a sample-pack.

3.2 COC Handling

3.2.1 Fill out the COC for each sample container (or multiple co-numbered VOA vials) as detailed in SOP ADMIN006. As a minimum, each COC must have the study number, sample number, chemicals to be analyzed, and the preparer's signature.

3.2.2 COCs for containers in sample-packs should also have the sample numbers of the other containers in the pack (replicates and field blanks) written in the Remarks section. Generally the primaries are the lowest sample numbers, then back-ups next, and finally the field blank as the highest number in the pack. Circle the sample number and type in the Remarks section to which the specific COC applies (i.e. Backup=004) and indicate the type of replicate or field blank at the top of the COC by writing a PI, BI, B2, FBI, etc. Check with the project leader for specific notation to be used to number and name replicates, Organize the COCs for the sample-pack from lowest to the highest sample number. Fold the COCs and place in a 6" x 12" plastic bag with the lowest sample number showing, then place the bag between the bottles within the sample-pack.

3.2.3 For storage-packs, the COCs should be filled-out as in 3.2.1. Then the COCs matching the labeled containers in the storage-pack should be simply stacked on top of the containers inside the box in sample number order. Primary, backup and field blank sample containers may not be designated until the samples are collected.

3.2.4 For VOA sample packs, fold and place the associated COCs in a 6" X 12" plastic bag with the lowest sample number visible. Then place the bagged COCs in the large bag with the VOA containers. Seal the large bag, label it as described in 3.3.3, and place it in a box with other VOA sample-packs for the same study. Label the box with the study number and the letters "VOA".

3.3 An Example of Sample-Pack Preparation

The following design is commonly used for well sampling

3.3.1 Obtain a sample-pack container suitable to the sample containers directed in the protocol, normally a polystyrene six-pack. Start with the narrow end of the six-pack facing you. Begin placing sample containers starting with the near left compartment. Continue placing containers in sequence in a clockwise direction (See diagram below). If there are less than six bottles

in the pack, leave the center compartments empty. When finished, the lowest numbered container (usually the primary) and the highest numbered container (field blank) should both be in the same end of the six-pack. See the diagram below.

PRIMARY 001	BACKUP1 002	BACKUP2 003
FIELD BLANK 006	BACKU P4 005	BACKUP3 004

SIX-PACK

3.3.2 Put the sample-pack, along with the associated COCs in a 24" X 24" plastic bag and close the top of the bag with a rubber band.

3.3.3 Label the large bag with the study number, the range of sample numbers inside, and other information required by the project leader. Use a permanent marker to write directly on the bag or on a white adhesive label.

3.4 An Example of Storage-Pack Preparation

3.4.1 To pack sample containers in storage-packs, turn the narrow end of the box toward you. Place the sample container in the near left compartment and continue placing the labeled containers in sequence down the row away from you. When a row is full, start again with the near compartment in the row immediately to the right, continuing until the box is full.

3.4.2 Use an adhesive label to mark the outside of the box with the study number and the range of sample container numbers inside. On the inside box flap, at the beginning of each row, list the range of sample numbers in that row.

3.4.3 Place the unfolded COCs in sequence from lowest to highest, on top of the sample containers and close up the box.

3.5 Storage

All prepared sample/storage-packs for a given study should be stored together on the shelves in the West Sacramento warehouse. The warehouse manager will direct the location of storage and whether to use a pallet or place the packs directly on the shelves. Place a removable label with the study number on the shelving to easily identify what containers are stored at each location.

4.0 STUDY SPECIFIC DECISIONS

If deviations from the standard operating procedures outlined above are required, they should be detailed in the study protocol. Before preparing any sample containers for a study, the project leader or field coordinator must review the protocol to determine:

4.0.1 The type of container.
4.0.2 The number of containers required including spares and quality control.
4.0.3 The number of packs to assemble
4.0.4 The type of sample-pack or storage-pack required.
4.0.5 Discrete label numbers to prevent confusion of sample results.
4.0.6 The appropriate COC form.
4.0.7 Additional container materials required such as aluminum foil or teflon sheets.

SUPPLEMENT 5
Analytical Methods

CALIFORNIA DEPT. OF FOOD AND AGRICULTURE
Center for Analytical Chemistry
Environmental Monitoring Section
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(916) 262-2080 Fax (916) 262-1572

Method #: 50.5
Original Date: 02/07/97
Revised:

The Determination of Triclopyr in Plant Materials

Scope: This method is for the analysis of triclopyr in acorn, bittercherry, bracken fern, buckbrush, deerbrush, deergrass, dogwood, elderberry, golden fleece and manzanita berry, soaproot, pearly everlasting, and willow. The reporting limit for bracken fern and manzanita berry is 0.03 ppm, golden fleece is 0.07 ppm and buck brush is 0.05 ppm.

Principle: The plant materials were chopped into small pieces and homogenized in a cuisinart with dry ice. Triclopyr was extracted from the ground sample by blending with benzene and sulfuric acid. An aliquot of the benzene extract was cleaned up by extracting with the sodium bicarbonate solution and ethyl ether. The extract was acidified with sulfuric acid. Methylene chloride was used to extract the residue from the acidified aqueous solution. The resulting extract was concentrated then derivatied with diazomethane and quantitated by GLC/ECD and GC/MSD

Reagents, Equipment and Instrument:

Reagents: All reagents must be suitable for pesticide residue analysis.

1. Solvent: Benzene (It is recognized as a carcinogen, review MSDS before handling), Ethyl Ether, Hexane, Methylene chloride, Iso-octane, pesticide grade or equivalent
2. Sulfuric acid (1:1), reagent grade
3. Sodium bicarbonate solution, 4% (w/v)
4. Triclopyr stock solution (1 mg/mL): Obtain standard from Standard Repository CDFA. 3292 Meadowview Rd. Sac., CA 95832.
5. Sodium Sulfate, anhydrous, granular (ACS)
6. Diazomethane (carcinogenic and explosive reagent, review MSDS before handling)
7. Dry ice

Equipment:

1. Nitrogen evaporator Organomation Model # 12
2. Rotary evaportor (Büchi/Brinkmann, R110)
3. Cuisinart™ food processor (Model DLC 7)
4. Sorvall® Omi-Mixer - pint mason jars
5. Separatory funnel, 500 mL
6. Flat-bottomed round flask, 500 mL
7. Graduated conical centrifuge tubes, 15 mL
8. Mixing cylinder, 100 mL
9. Filter paper, Whatman # 1

Reagent, Equipment and Instrument: continued

Instrument:

1. Hewlett Packard Gas Chromatograph Model 6890 with autosampler and a electron capture detector (ECD).
2. Hewlett Packard Gas Chromatograph Model 6890 with autosampler and a mass selective detector (MSD).

Analysis:

Sample Extraction:

1. Cut entire plant sample into small pieces. Grind the sample in a Cuisinart with dry ice until the sample becomes homogeneous.
2. Transfer the ground sample to a mason jar cover it with a piece of aluminum foil and apply lid loosely. Store in a freezer overnight to allow carbon dioxide to dissipate.
3. Weigh 40 g of ground elderberry, 35g of acorn, bracken fern, deerbrush, deergrass, dogwood, manzanita berry, willow, or 20g of bitterrcherry, golden fleece, soaproot, or 15g of buckbrush, or 10 g of pearly everlasting plant sample into a pint size mason jar. Then add 100 mL of benzene and 1.5 mL of 1:1 sulfuric acid.
4. Blend with Omi-mixer for 4 minutes at a setting of 3:5.
5. Filter the extract through a funnel lined with # 1 Whatman filter paper containing 10 g sodium sulfate into a graduate mixing cylinder.
6. Remove a 50 mL aliquot of extract from the cylinder to a 500 mL separatory funnel.
7 Extract with 200 mL of 4% sodium bicarbonate solution by shaking for 1.5 minute, venting often to relieve pressure. Drain lower aqueous layer into a 600 mL beaker.
8. Add another 100 mL of sodium bicarbonate soln. to separatory funnel and shake 1 minute. Add lower aqueous layer to the beaker and discard benzene in a proper waste container.
9. Pour contents of beaker back into separatory funnel and add 100 mL ethyl ether. Shake gently for 1 minute and vent often.
10. Drain aqueous layer into the beaker and discard ether.
11. Add 3 mL of 1:1 sulfuric acid to aqueous extract carefully and swirl. **Beware-- there will be foaming!** Continue adding sulfuric acid until aqueous soln. is acidic (~ 10 mL) and foaming stop.
12. Pour acidifed aqueous solution back into separatory funnel.
13. Add 100 mL methylene chloride and shake vigorously for 1 minute.
14. Allow layers to separate. Drain the organic layer into a 500 mL flask.
15. Repeat steps 12 and 13 two more times using 80 mL methylene chloride.
16. Add 5 mL of iso-octane to the flask.
17. Rotoevaporate the extract to ~ 4 mL at 35 °C under approximately 15 inches of Hg vacuum.
18. Add 1 mL diazomethane solution into the flask. Cover the flask with aluminum foil and swirl it gently. Allow the reaction mixture to stand in a fumehood for 30 minutes. (If the brownish-yellow color has disappeared within 30 minutes, add additional diazomethane solution and let the reaction mixture stand for another 30 minutes.)
19 Evaporate the solvent and the excess reagent to just dryness at ambient temperature using a gentle stream of nitrogen.
20. Pipet 5 mL of hexane into flask and swirl. Transfer the extract immediately to an autosampler vial for GLC analysis.

Analysis: continued

Instrument Condition:

Primary Analysis:

Hewlett Packard 5890 GC with ECD
Column: HP-1 (Crosslinked methyl silicone gum) 30 m x 0.53 mm x 0.88 µm
Carrier gas: Helium, column flow rate 1.5 mL/min
Injector temperature: 220 °C
Detector temperature: 300 °C
Column oven temperature:

Ramp 1	Initial temperature:	150 °C hold for 2 min
	Rate:	5 °C / min
Ramp 2	Initial temperature	190 °C
	Rate	30 °C / min
	Final temperature	250 °C hold for 4 min

Injection volume: 1 µL
Retention times: 8.420 ± 0.10 min

Confirmation Analysis:

Hewlett Packard 6890 gas chromatograph with mass selective detector (MSD).
Column: HP-Utra-1 25 m x 0.2 mm x 0.33 µm
Carrier gas: Helium, flow rate: 1 mL/min Constant Pressure
Injector temperature: 250 °C
Detector temperature: 280 °C
Column oven temperature:

Initial temperature:	70 °C hold for 1.5 min
Ramp rate:	20 °C / min
Final temperature	250 °C hold for 2 min

Purge: Initial off
On time 0.5 minute
Acquisition Parameters: 271.1,212.1,210.0
Run table Time 6.0 min mass spec on
Time 12 min mass spec off
Injection volume: 1 µL
Retention time: 9.66 ± 0.10 min

Calculations:

$$ppm = \frac{\text{(Peak height of sample) x (Std conc) x (Std vol. injected) x (Initial Vol) x (Final Vol of sample)}}{\text{(Peak height of Std) x (Sample vol injected) x (Sample weight (g)) x (aliquot Vol.)}}$$

Method Performance:

Quality Control:

1. A four-point calibration curve of 0.1, 0.25, 0.5 and 1.0 ηg/µL triclopyr was obtained at the beginning and the end of each set of samples.

Method Performance: continued

Quality Control:

2. Each sample was analyzed two times to insure reliability of the chromatography. If the signal of the sample was greater than that of the highest concentration of the calibration curve, the sample was diluted within the calibration range and reanalyzed.
3. For each set of samples, one matrix blank and one matrix spike were included, and each set of samples did not contain more than twelve samples.
4. Positive sample result was confirmed by MSD.

Method Detection Limit (MDL)

Method Detection Limit refers to the lowest concentration of analyte that a method can detect reliably in either a sample or blank. This was determined by fortifying seven aliquots of background sample matrix with 5 ug of triclopyr and processing through the entire method along with a blank. The standard deviation derived from the 7 spiked samples was used to calculate the MDL using the following equation:

$$\mathbf{MDL} = t\,S$$

where:

t is the Students' t value for the 99% confidence level with n-1 degrees of freedom (n-1, 1 - α = 0.99), which is 3.143. n represents the number of replicates.

S denotes the standard deviation obtained from replicate analyses.

Results of the standard deviation and the MDL are in appendix 1.

Reporting Limit (RL):

It refers to the level above which quantitative results may be obtained.

The sample size, MDL and RL for each matrix were tabulated as follow:

Matrix	Sample size (g)	MDL (ppm)	RL (ppm)
Acorn	35	0.01	0.01
Bittercherry	20	0.066	0.07
Bracken Fern	35	0.0147	0.03
Buck Brush	15	0.049	0.05
Deerbrush	35	0.0197	0.03
Deergrass	35	0.045	0.05
Dogwood	35	0.023	0.03
Elderberry	40	0.01	0.01
Golden Fleece	20	0.07	0.07
Manzanita berry	35	0.022	0.03
Pearly Everlasting	10	0.065	0.07
Soaproot	20	0.027	0.03
Willow	35	0.03	0.03

Method Performance: continued

Recovery Data:

Method validation was performed by spiking the background plants; bracken fern, buckbrush, golden fleece and manzanita berry, with three different levels (0.3, 3.0, and 30 ppm) of triclopyr for three replicates.

Results of the method validation are summarized in appendix II.

Discussion:

The sample sizes of this method varied in different plant matrices, because some of the plant matrices contain oil or other unknown materials which interfered with the analysis. A sample size of 35 g was used for most of the matrices. Buckbrush sample size was decreased due to the imitation of background matrix during the determination of the MDL.

References:

Determination of Phenoxies in Vegetation, Pesticide Residue Laboratory Method, Center for Analytical Chemistry, California Dept. of Food and Agriculture.

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Catherine Cooper

TITLE: Agricultural Chemist III Supervisor

APPENDIX I *Triclopyr Spike Results (ppm) for MDL Determination*

Spike	Acorn	Bittercherry	Bracken Fern	Buckbrush	Deerbrush
1	0.096	0.202	0.108	0.140	0.101
2	0.089	0.178	0.115	0.133	0.112
3	0.096	0.199	0.106	0.159	0.099
4	0.095	0.228	0.112	0.132	0.112
5	0.092	0.202	0.103	0.132	0.111
6	0.094	0.236	0.104	0.118	0.106
7	0.091	0.186	0.103	0.110	0.116
SD	0.003	0.021	0.005	0.016	0.006
MDL	0.010	0.066	0.015	0.050	0.020

Spike	Deergrass	Dogwood	Elderberry	Golden Fleece	Soaproot
1	0.219	0.116	0.096	0.150	0.226
2	0.213	0.120	0.090	0.144	0.164
3	0.233	0.128	0.096	0.170	0.224
4	0.257	0.126	0.095	0.185	0.221
5	0.241	0.107	0.092	0.165	0.220
6	0.231	0.119	0.094	0.210	0.234
7	0.237	0.111	0.091	0.160	0.240
SD	0.015	0.008	0.002	0.022	0.008
MDL	0.046	0.023	0.008	0.070	0.027

Spike	Willow	Manzanita Berry	Pearly Everlasting
1	0.116	0.111	0.202
2	0.122	0.112	0.178
3	0.116	0.110	0.199
4	0.106	0.112	0.228
5	0.099	0.130	0.202
6	0.110	0.115	0.236
7	0.096	0.116	0.186
SD	0.010	0.007	0.021
MDL	0.300	0.022	0.066

APPENDIX II *Method Validation Results*

	Bracken Fern		Buckbrush	
Spike Level (ppm)	Result (ppm)	Recovery (%)	Result (ppm)	Recovery (%)
0.3	0.247	82.3	0.260	86.7
	0.214	71.3	0.278	92.7
	0.230	76.7	0.246	82.0
3.0	2.30	76.6	2.36	78.8
	2.19	73.1	2.55	85.1
	2.57	85.7	2.69	89.8
30	24.0	80.1	26.9	89.8
	22.4	74.8	26.2	87.4
	23.9	79.9	24.9	83.2

	Golden Fleece		Manzanita Berry	
Spike Level (ppm)	Result (ppm)	Recovery (%)	Result (ppm)	Recovery (%)
0.3	0.202	67.3	0.240	80.0
	0.190	63.3	0.305	102
	0.238	79.3	0.243	81.0
3.0	2.01	67.1	2.52	83.4
	1.88	62.8	2.69	89.7
	2.11	70.2	2.44	81.2
30	22.1	73.6	24.3	81.0
	20.3	67.7	28.2	93.8
	22.8	76.0	25.2	84.2

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

Project No.	191-North Coast Forest-Yurok-Vegetation	Lab	CDFA
Lab Project Manager	Cathy Cooper	Phone	262-2080
Project Chemist	J. Hsu/J. White	Phone	262-2074
EHAP Project Manager	Pam Wofford	Phone	324-4297
EHAP Lab Liaison/ QA Officer	Carissa Ganapathy	Phone	322-3082

Type of Analysis:

Sample Type	Analysis For	Reporting Limit	Number of Samples
Please see attachment for plant schedule and need for validation			Up to 30 samples per veg type

All samples will be for total, not dislodgeable

Methods Development: See attachment
Sample Storage: All samples to be kept frozen until extracted.
Sample Extraction: All extracts to be kept frozen until analyzed.
Analytical Standard Source: Normal sources
Instrumentation:
Confirmation Method: none
Continuing QC: See attachment
Sample Disposition: Return unused portion of sample to EHAP warehouse
Extract Disposition: Comply with GLP requirements
Reporting/Turnaround: See attachment
Cost of Analysis: See attachment

Other Specifications:

Field sampling could begin in late April or early May of 2000

Use provided background vegetation for all quality control analyses.

Approved by: Pam Wofford 5/3/00 Catherine Cooper 4/25/00
CDPR Representative Lab Representative Date

Carissa Ganapathy 4/24/00
lab liaison

LBSPEC191

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

METHODS DEVELOPMENT AND VALIDATION

Specifications **Validation***

Method # CDFA lab # 50.5
Sample Matrix: Maidenhair fern
Analyzed For: triclopyr/2,4-D
Reporting Limit: approximately 0.05-0.07ppm
Other Specifications:

	Sample Type	Spike Level	# Reps
1	vegetation on page 1	0.3, 3.0, 30 ppm	5 each level
2			
3			
4			
5			

Method # CDFA lab # 50.5
Sample Matrix: Possible new plants in summer
Analyzed For: triclopyr/2,4-D
Reporting Limit: approximately 0.05-0.07ppm
Other Specifications:

	Sample Type	Spike Level	# Reps
1	vegetation on page 1	0.3, 3.0, 30 ppm	5 each level
2			
3			
4			
5			

Method #
Sample Matrix:
Analyzed For:
Reporting Limit:
Other Specifications:

	Sample Type	Spike Level	# Reps
1			
2			
3			
4			
5			

* Each laboratory shall determine a method detection limit (MDL), instrument detection limit (IDL) and a reporting limit (RL) for each analyte. Each laboratory shall also document their terms, definitions and procedures for determining MDL, IDL and RL in their approved analytical method. Each laboratory shall provide a copy of their approved analytical method before analyzing any field samples.
The results from the method validation study will be used to establish recovery control limits for the field study.

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

CONTINUING QUALITY CONTROL

Reagent or Solvent Blanks: 1 blank matrix per extraction set
Reagent or Solvent Spikes:
Blank-Matrix Spikes: 2 matrix spike duplicates per extraction set
Matrix: all vegetation types/all chemicals — Spike Level: **3.0 ppm**
Matrix: — Spike Level:
Matrix: — Spike Level:
Matrix: — Spike Level:
Actual Matrix Spikes:
Replicate Matrix Analyses:
Replicate Extract Injections:
Confirmation Analyses:

QC analysis: QC sample recoveries will be compared to control limits determined by validation data.
QC will be examined according to SOP QAQC001.00

Samples to be Analyzed

Primary Samples: All primary samples to be analyzed
Backup Samples:
Field Blank Samples:

Storage Dissipation Study: Triclopyr storage stability completed for similar vegetation

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

REPORTING PROCEDURES

Completing the Chain of Custody Record:

1. Sign and date the box marked "Received for Lab by:".
2. Write in the Lab I.D. number in the appropriate space.
3. Results should be reported as follows:

All detections to be reported as ppm on a fresh weight basis.

4. For those samples which contain no detectable amount write "none detected" and indicate the reporting limit.
5. The chemist who analyzed the sample should sign and date in the appropriate space.
6. Write in the date of extraction and analysis in the appropriate space.

See attached Chain of Custody for an example.

Turnaround Time: All samples to be extracted within ~~14~~ 21 days of date of sampling. — Time extended to complete MDL and validation when samples arrive

Additional Specifications:

When?	Veg type	Chemical	completed validation (for total)?	R.L.
Spring	Willow	Triclopyr/2,4-d	yes	0.05
	Maidenhair Fern	Triclopyr/2,4-d	working on now	
	Bear Grass	Triclopyr/2,4-d	yes	0.05
Fall	Bear Grass	Triclopyr/2,4-d	yes	0.05
	Huckleberry	Triclopyr/2,4-d	yes	0.05
	Oregon Grape Root ~~or stems~~	Triclopyr/2,4-d	no	
	Yarrow	Triclopyr/2,4-d	no	
	Acorn	Triclopyr/2,4-d	yes	0.05
	Willow	Triclopyr/2,4-d	yes	0.05
	Manzanita Berry	Triclopyr/2,4-d	yes	0.05
	Maidenhair Fern	Triclopyr/2,4-d	working on now	
	Ground Berry	Triclopyr/2,4-d	no	
Fall	Bear Grass	Glyphosate?	no	
	Huckleberry	Glyphosate?	no	
	Oregon Grape Root or stems	Glyphosate?	no	
	Yarrow	Glyphosate?	no	
	Acorn	Glyphosate?	yes	0.12
	Willow	Glyphosate?	yes	0.1
	Maidenhair Fern	Glyphosate?	yes	0.1
	Manzanita Berry	Glyphosate?	yes	0.1
	Ground Berry	Glyphosate?	no	

Glyphosate applications may not occur in the fall.
Triclopyr/2,4-D applications will occur in the spring and fall.
Some of the matrices have mdl determination but not validated.

SUPPLEMENT 6
EHAP Standard Operating Procedure QAQC001.00
Chemistry Laboratory Quality Control

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
1020 N Street
Sacramento, CA 95814

STANDARD OPERATING PROCEDURE
Chemistry Laboratory Quality Control

KEY WORDS

QC; method detection limit; MDL; reporting limit; RL; confirmation; verification; AB 2021; method development; method validation; storage stability; split; spike; blank; laboratory specifications

APPROVALS

APPROVED BY: John S. Sanders — Management — DATE: 7/31/95

APPROVED BY: Heinz L. Blum — EHAP Senior Scientist — DATE: 7/31/95

APPROVED BY: Randy Segawa — EHAP Quality Assurance Officer — DATE: 7/28/95

PREPARED BY: Randy Segawa — DATE: 7/28/95

Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

1.2.7 **Extraction Set** refers to a single group of samples extracted and processed at the same time.

1.2.8 **Instrument Detection Limit (IDL)** is 1 - 5 times the signal-to-noise ratio depending on the analytical method.

1.2.9 **Method Detection Limit (MDL)** refers to the USEPA definition (40 CFR, Part 136, Appendix B). "The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix...."

1.2.10 **Reporting Limit (RL)** is 1 - 5 times the MDL depending on the analytical method and matrix. The MDL can vary from sample to sample because of matrix effects. Ideally, the RL will not change, will be set high enough to account for matrix effects, yet low enough to be useful.

1.2.11 **Spike** refers to a known amount of pesticide added. These QC samples are used to check the precision and accuracy of a method.

1.2.12 **Split** refers to one homogeneous sample divided into several aliquots, with the different aliquots analyzed by different laboratories. These QC samples are used to check the specificity and precision of a method.

1.2.13 **Standard** refers to the laboratory analytical standard.

2.0 GENERAL PROCEDURES

These guidelines are meant to be a starting point; a specific study may require more or less QC than is given here. The procedures outlined here are the QC measures which should be reported. Performing other QC procedures such as frequency of standard injections and calibrations are left to the chemist's discretion.

2.1 General Method Development

Many times the method development will be a negotiation between the project leader and the laboratory. The project leader can suggest some method perfomance goals (e.g., specificity, reporting limit, etc.), but the goals need to be balanced with laboratory cost and time constraints. The, method performance should be consistent with the study objectives.

2.1.1 *Standard* - Standard solutions should be validated prior to use by checking for chromatographic purity or verification of the concentration using a second standard prepared at a different time or obtained from a different source.

2.1.2 Method Detection Limit Determination - The MDL is determined by the USEPA method (40 CFR, Part 136, Appendix B). The complete procedure is given in Appendix 1. Briefly, the MDL is determined by analyzing at least 7 low-level matrix spikes (generally 1 - 5 times the IDL) and performing the following calculation:

$$MDL = t \times S$$

where:

t = Student's t value for 99% confidence level (l-tailed) and n-l degrees of freedom
S = standard deviation

2.1.3 Reporting Limit Determination - The RL is determined by the chemist and set at 1 - 5 times the MDL depending on the matrix and instrument.

2.1.4 Method Validation - At the onset of a study, an acceptable range of spike recoveries will be established. This range will be established by analyzing blank-matrix spike samples. Two to five replicate analyses at two to five different spike levels will be used to determine the mean percent recovery and standard deviation. Number of replicates and spike levels will be chosen by the project leader. Warning limits will be established at the mean percent recovery plus/minus 1 - 2 times the standard deviation. Control limits will be established at the mean percent recovery plus/minus 2 -

3 times the standard deviation. Any subsequent spiked samples outside the control limits may require the set of samples associated with that spike to be reanalyzed.

2.1.5 Storage Stability - Storage stability needs to be evaluated on a case-by-case basis, so no specific test design is specified. However, in general the test should be run for the longest anticipated holding period, with at least four sampling intervals and two replicate samples at each sampling interval. Other factors may also need to be incorporated into the storage stability tests, such as pH, temperature, and container type. The project leader is responsible for specifying the design of the storage stability test.

2.2 General Continuing QC - These analyses are to be done by the main lab on a continuing basis. Each extraction set should consist of 5-20 actual samples. Exact frequency of QC analyses and spike levels are chosen by the project leader.

2.2.1 Reagent Blanks - 1 - 2 per extraction set

2.2.2 Blank-Matrix Spikes - 1 - 3 per extraction set

2.2.3 Analytical Confirmation - 0 to 100% (normally 10%) of positive samples confirmed

2.2.4 Split Matrix Samples - 0 to 100% (normally 10%) of the actual samples should be split into two aliquots, one aliquot analyzed by the main lab, and one by the QC lab. For studies that cannot have actual samples split or for which only a few positives are anticipated, blind spike samples may be used.

2.2.5 Blind Spikes - 0 to 100% (normally 10%) of the actual samples should be accompanied by laboratory-spiked samples disguised as real samples. These should be done only for matrices that can be accurately spiked.

2.3 Optional Continuing QC - The following analyses should be considered but may not be routinely performed unless specified by the project leader.

2.3.1 Internal Standard - a chemical not expected in the samples can be spiked into all samples or extracts. This is particularly useful for quantifying mass spectrometry data.

2.3.2 Replicate Sample Analyses - analyzing multiple aliquots of a single sample will give a better estimate of the method precision.

2.3.3 Replicate Extract Analyses - multiple analyses of a single extract will give a separate estimate of the precision of the extraction and analysis processes.

2.3.4 Split Extract Analyses - analyzing a single extract with more than one lab is useful for checking discrepancies between laboratories.

2.3.5 Reference Material - a stable sample that contains the analyte(s) of interest and has been analyzed many times so that the concentration(s) are known. Analysis of this material may give a better estimate of the method's accuracy than spiked samples. Also useful for method development.

2.3.6 Standards Exchange - exchanging analytical standards between the primary and QC lab is useful for checking discrepancies in split samples.

3.0 WELL WATER STUDY QC PROCEDURES

3.1 Well Water Study Method Development - The general method development procedures should be used.

3.2 Well Water Study Continuing QC - The following specific continuing QC should be used in place of the general continuing QC:

3.2.1 Reagent Blanks - 1 to 2 per extraction set

3.2.2 Blank-Matrix Spikes - 1 to 3 per extraction set

3.2.3 AB 2021 confirmation and verification - at least one additional sample' from the same well must be analyzed by a second lab or a second method for each positive sample. AB 2021 confirmation requires positive detection in at least 2 discrete samples and verification with a second lab or a second method:

3.2.4 Blind Spikes - 1 blind spike should be submitted for every 3 - 50 well samples.

3.2.5 Field Blanks - 1 field blank should be collected at each well, but analyzed only if the well sample is positive.

4.0 AIR STUDY QC PROCEDURES

4.1 Air Study Method Validation (trapping efficiency) - In addition to the general procedures, the trapping efficiency should be determined. This normally involves collecting a series of 2-stage air samples. The top stage sampling tube contains glass-wool and is spiked. The bottom stage consists of the normal sampling tube. The 2-stage sample is placed on an air sampler and run for the appropriate amount of time. Both stages are then analyzed to determine the proportion of the spike trapped in the bottom stage. The test should consist of two to five replicate analyses at two to five spike levels. Samplers should run for various lengths of time, if necessary. To determine the precision of the spiking technique, five sample tubes with glass wool should be spiked and analyzed. Oxidation products should also be analyzed to determine the rate of conversion. Exact test specifications are chosen by the project leader.

4.2 Air Study Continuing QC - In addition to the general procedures, one reagent spike should be analyzed with each extraction set. The air sampling matrix will occasionally give an enhanced detector response.

In general, it is not possible to split air samples, so split matrix analyses are not usually done.

5.0 CALCULATIONS

5.1 Calculating the Method Detection Limit - The MDL is determined by performing the following calculation:

$$MDL = t \times S$$

where:

t = Students t value for 99% confidence level (I-tailed) and n-I degrees of freedom
S = standard deviation

5.2 Calculating Warning and Control Limits - The method validation data are used to set warning and control limits. Warning limits will be established at the mean percent recovery plus/minus 1 - 2 times the standard deviation. Control limits will be established at the mean percent recovery plus/minus 2 - 3 times the standard deviation. Any subsequent spiked samples outside the control limits may require the set of samples associated with that spike to be reanalyzed.

6.0 REPORTING REQUIREMENTS

These reporting requirements pertain only to the QC data. There may be other reporting requirements specified in the EHAP Analytical Laboratory Specifications Form (Appendix 2).

6.1 Reporting Method Development Results - The following should be reported by the lab to the EHAP QA officer prior to the start of any field sample analyses: the spike level and concentration detected for each sample of the MDL determination, the method validation, and the storage stability. The EHAP QA officer will review, summarize and submit the data to the project leader.

6.2 Reporting Continuing QC Results - The following QC results should be reported by the lab to the EHAP QA officer on a continuous basis: the concentration of all blanks, the concentration detected for all spikes, the amount added for all spikes. Any spiked samples outside the control limits may require the set of samples associated with that spike to be reanalyzed. The **EHAP** QA officer will

review, summarize and submit the data to the project leader. In addition, the project leader may request to be notified if any problems arise during the course of chemical analysis.

6.3 Reporting Sample Results - The laboratory should not use any spike or blank data to adjust the field sample results, unless specified by the project leader. Any adjustments should be made by EHAP personnel.

7.0 STUDY-SPECIFIC DECISIONS

The project leader is responsible for the following specific decisions for each individual study. These decisions must be made for both the primary lab and the QC lab, if one is used. All decisions should be given to the EHAP QA officer who will document the decisions and transmit them to the lab using the EHAP Analytical Laboratory Specifications Form.

7.1 Method performance goals - reporting limit, specificity, precision, accuracy, sample size, time to complete analysis, etc.

7.2 Number of MDL spike samples

7.3 Method validation spike levels and number of replicates

7.4 Warning and control limit criteria (1 - 3X standard deviation)

7.5 Storage stability test design

7.6 Number or frequency of continuous QC spike analyses

7.7 Concentration of continuous QC spike samples

7.8 Number or frequency of analytical confirmation

7.9 Number or frequency of split analyses

7.10 Use, selection and concentration of an internal standard

7.11 Number or frequency of replicate sample analyses

7.12 Number or frequency of blind spike analyses

7.13 Concentration of blind spike samples (also select analyte(s) if multi-residue method)

7.14 Number or frequency of replicate extract analyses

7.15 Number or frequency of split extract analyses

7.16 Number or frequency of standard reference material analyses

7.17 Method of AB 2021 verification - 2nd lab or 2nd method

7.18 Trapping efficiency test design

7.19 Number or frequency of reagent spike analyses

8.0 REFERENCES

California Department of Pesticide Regulation. 1988. Chemistry Laboratory Quality Control Guidelines. Environmental Hazards Assessment Program.

Segawa, R. 1993. AB 2021 Confirmation and Verification Policy. Memorandum to Kean Goh, dated November 22, 1993. Environmental Hazards Assessment Program.

APPENDIX 1 - U.S. EPA Method Detection Limit Determination

APPENDIX 2 - Analytical Laboratory Specifications

APPENDIX 1

APPENDIX B TO PART 136—DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD DETECTION LIMIT—REVISION 1.11

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a signifi-

cantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2 \Big/ n\right]$$

$$S = (S^2)^{1/2}$$

where:

X_i; i=1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from i=1 to n.

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1,1-\alpha\,=\,0.99)} \quad (S)$$

where:

MDL = the method detection limit

$t_{(n-1,1-\alpha\,=\,.99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2/df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B<3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S^2_A + 6S^2_B}{12}\right]^{1/2}$$

if $S^2_A/S^2_B>3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

$$MDL = 2.681\ (S_{pooled})$$

where 2.681 is equal to $t_{(12,\ 1-\alpha\,=\,.99)}$.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from precentiles of the chi squared over degrees of freedom distribution.

LCL=0.72 MDL

UCL=1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLES OF STUDENTS' t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1,\ .99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which

affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

[49 FR 43430, Oct. 26, 1984; 50 FR 694, 696, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986]

Appendix C to Part 136—Inductively Coupled Plasma—Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes Method 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See Section 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See Section 5.)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instruction provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 *Dissolved*—Those elements which will pass through a 0.45 μm membrane filter.

3.2 *Suspended*—Those elements which are retained by a 0.45 μm membrane filter.

3.3 *Total*—The concentration determined on an unfiltered sample following vigorous digestion (Section 9.3), or the sum of the dissolved plus suspended concentrations. (Section 9.1 plus 9.2).

3.4 *Total recoverable*—The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 9.4).

3.5 *Instrumental detection limit*—The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 *Sensitivity*—The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

3.7 *Instrument check standard*—A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 7.6.1)

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

Project No. _____ Lab _____
Lab Project Manager _____ Phone _____
Project Chemist _____ Phone _____
EHAP Project Manager _____ Phone _____
EHAP Lab Liaison/ QA Officer _____ Phone _____

Type of Analysis:

	Sample Type	Analysis For	Reporting Limit	Number of Samples
1				
2				
3				
4				

Methods Development: See attachment
Sample Storage: _____
Sample Storage: _____
Sample Extraction: _____
Analytical Standard Source: _____
Instrumentation: _____
Confirmation Method: _____
Continuing QC: See attachment
Sample Disposition: _____
Extract Disposition: _____
Reporting/Turnaround: See attachment
Cost of Analysis: See attachment

Other Specifications:

_____
_____
_____
_____
_____
_____
_____

Approved by: _____ _____ _____
CDPR Representative Lab Representative Date

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

METHODS DEVELOPMENT

Specifications			Validation*	
Method # ________				
Sample Matrix: ________		Sample Type	Spike Level	# Reps
Analyzed For: ________	1			
Reporting Limit: ________	2			
Other Specifications: ________	3			
________	4			
________	5			
________				
________				

Specifications			Validation*	
Method # ________				
Sample Matrix: ________		Sample Type	Spike Level	# Reps
Analyzed For: ________	1			
Reporting Limit: ________	2			
Other Specifications: ________	3			
________	4			
________	5			
________				
________				

Specifications			Validation*	
Method # ________				
Sample Matrix: ________		Sample Type	Spike Level	# Reps
Analyzed For: ________	1			
Reporting Limit: ________	2			
Other Specifications: ________	3			
________	4			
________	5			
________				

* Each laboratory shall determine a method detection limit (MDL), instrument detection limit (IDL), and a reporting limit (RL) for each analyte. Each laboratory shall also document their terms, definitions, and procedures for determining MDL, IDL, and RL in their approved analytical method. Each laboratory shall provide a copy of their approved analytical method before analyzing any field samples. The results from the method validation study will be used to establish recovery control limits for the field study.

ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

CONTINUING QUALITY CONTROL

Reagent or Solvent Blanks
Reagent or Solvent Spikes
Blank-Matrix Spikes
Matrix Spike Level
Matrix Spike Level
Matrix Spike Level
Matrix Spike Level
Actual Matrix Spikes
Replicate Matrix Analyses

Replicate Extract Injections

Confirmation Analyses

For Well Samples:

Primary Samples
Backup Samples
Field Blank Samples

Storage Dissipation Study

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

REPORTING PROCEDURES

Completing the Chain of Custody Record:

1. Sign and date the box marked "Received for Lab by:".
2. Write in the Lab I.D. number in the appropriate space.
3. Results should be reported as follows:

4. For those samples which contain no detectable amount write "*none detected*" and indicate the reporting limit.
5. The chemist who analyzed the sample should sign and date in the appropriate space.
6. Write in the date of extraction and analysis in the appropriate space.

See attached Chain of Custody for an example.

Turnaround Time:

Additional Specifications:

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

BUDGET

Contract #:_____

Analysis	Number of Analyses	Cost per Analysis	cost

Total Cost = _____

Please send all reports and invoices to:

Attn:
California Department of Pesticide Regulation
1020 N Street, Rm. # 161
Sacramento, California 95814-5604

SUPPLEMENT 7
EHAP Standard Operating Procedure QAQC004.01
Transporting, Packaging and Shipping Samples from the Field to the Warehouse or Laboratory

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
830 K Street, Suite 200
Sacramento, California 95814

STANDARD OPERATING PROCEDURE

Transporting, Packaging and Shipping Samples from the Field to the Warehouse or Laboratory

---

KEY WORDS-
Ice chest, sample, ice, temperature

APPROVALS

APPROVED BY: _____ DATE: 9/25/99
Kean S. Goh, Management

APPROVED BY: _____ DATE: 9/7/99
Lisa Ross, EHAP Senior Scientist

APPROVED BY: _____ DATE: 9/7/99
Carissa Ganapathy, EHAP Quality Assurance Officer

REVISED BY: _____ DATE: 8/2/99
DeeAn Jones, Environmental Research Scientist

Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE
Transporting, Packaging and Shipping Samples from the Field to the Warehouse or Laboratory

1.0 INTRODUCTION

1.1 Purpose

To ensure that samples are adequately packed in the field to avoid breakage and that samples are stored at the appropriate temperature for each media.

1.2 Scope

This document will provide specific instructions for packing and transporting samples after they have been collected. For instructions on how to package sampling materials prior to collection, see Standard Operating Procedure QAQC005.00.

2.0 MATERIALS

2.1 Ice chests
2.2 Wet ice or blue ice for cooling water or vegetation samples
2.3 Dry ice for cooling soil, air, or vegetation samples
2.4 Appropriate packing material for sample containers (ex: styrofoam 6-packs for quart jars and 1 L Amber bottles)
2.5 Hobo® Temp data logger or Min/Max Temperature recorder
2.6 Bubble plastic or other packaging material
2.7 Duct tape or packing tape
2.8 Permanent black marker
2.9 White label tape

3.0 PROCEDURES

3.1 SAMPLE TRANSPORT FROM THE FIELD TO THE WAREHOUSE OR LABORATORY

Before leaving the warehouse (sometime prior to sample collection), an ice chest should be filled with the appropriate ice (wet, dry, blue). This is to ensure that the samples are chilled immediately after collection. If the study is conducted under Good Laboratory Practices, a Hobo® Temp data logger or Min/Max Temperature recorder should be placed in each ice chest. Instructions for operating a Hobo® Temp data logger are found in Standard Operating Procedure EQOT001.01.

3.1.1 Place samples in styrofoam holders or other containers in ice chests immediately after sampling in the field or removal from storage refrigerators or freezers at an Environmental Hazards Assessment Program warehouse facility.

3.1.2 Surround the samples with sufficient ice to chill to the appropriate temperature. For **water samples** and **vegetation to be analyzed for internal and/or dislodgeable residue**, use wet ice or blue ice to chill the samples to 4°C. For **air**, **soil**, and **vegetation to be analyzed for total residue** use dry ice to chill the samples to -10°C to -70°C. It is preferable to maintain total pesticide residue samples at -70°C. If dry ice is not available, use any form of refrigeration in the following order of desirability: 1) freezer, 2) refrigerator, 3) blue ice, 4) wet ice (Sava, 1994). If the study is conducted under Good Laboratory Practices, the time and date the samples were placed in the ice chest should be recorded in the field notebook.

3.1.3 Check the samples often, making sure there is enough ice to maintain the required temperature. Add more ice when necessary, and drain off water as wet ice melts.

3.2 ADDITIONAL SHIPPING PROCEDURES

3.2.1 Pack samples securely by either adding packing material or wrapping containers in bubble plastic in order to prevent breakage.

3.2.2 Chain of custody (COC) records must accompany samples at all times and should be filled out according to Standard Operating Procedure ADMN006. Secure COCs in plastic bags and tape to the inside of the ice chest lid.

3.2.3 Using duct or packing tape, wrap the ice chest twice to seal the opening. This will alert the sample custodians to whether or not the ice chest has been tampered with.

3.2.4 If the ice chest is not already labeled, use the permanent marker and label tape to address the package to the appropriate destination. Note: Certain shipping companies may require a specific label to be used. Also, check with the airline or shipping company for any restrictions, including type of ice to be used.

3.3 RECEIVING

Samples that have been shipped to the West Sacramento warehouse, will be received by a sample custodian. This custodian will follow Standard Operating Procedure QAQC003.01 for check-in and check-out methods. Additionally, the custodian will notify the EHAP QA officer and project leader of any samples broken during transport and record the condition on the corresponding COC.

4.0 REFERENCES

Sava, R. 1994. Guide to Sampling Air, Water, Soil, and Vegetation for Chemical Analysis. Department of Pesticide Regulation - EHAP report EH 94-04. Sacramento, California.

SUPPLEMENT 8
EHAP Standard Operating Procedure QAQC003.01
Sample Tracking Procedures

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
830 K Street
Sacramento, CA 95814

STANDARD OPERATING PROCEDURE
Sample Tracking Procedures

KEY WORDS

Sample Tracking, Sample Tracking Database, Chain-of custody, Sample

APPROVALS

APPROVED BY: _____ DATE: 7/26/99
Management

APPROVED BY: _____ DATE: 7/19/99
EHAP Senior Scientist

APPROVED BY: _____ DATE: 7/15/99
EHAP Quality Assurance Officer

PREPARED BY: Andrea Hoffman, Johanna Walters DATE: 7/15/99 7/7/99

Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMIN002

STANDARD OPERATING PROCEDURE
Sample Tracking Procedures

1.0 INTRODUCTION

1.1 Purpose

This Standard Operating Procedure (SOP) discusses sample check-in and check-out procedures; the recording of chemistry data; sample disposal procedures; and the Sample Tracking Database.

1.2 Definitions

1.2.1 **Sample** is any environmental substance collected and analyzed for chemical content, toxicity, soil texture analysis, etc.

1.2.2 **Sample Tracking Database** is a relational database designed in Microsoft Access to trace a sample from the time it is checked into the storage facility until the sample is submitted to a laboratory for analysis or disposed of after a study is completed.

1.2.3 **Chain-of-custody** is a record describing in detail all pertinent information specific to each sample, including dates and signatures of persons handling the sample.

1.2.4 **Sample Custodians** are personnel, under direction of the lab liaison, responsible for receiving samples from field staff, delivering samples to the laboratory, and tracking samples in the Sample Tracking Database.

2.0 SAMPLE TRACKING

2.1 Sample Tracking Codes

Sample tracking codes are abbreviations for fields in the database that refer to specific information about each sample. The study number in combination with the sample number is identified as the key field and all information specific to the sample is referenced by the following codes back to the key field.

STANDARD OPERATING PROCEDURE
Sample Tracking Procedures

SAMPLE CODES:

P= Primary	R= Replicate	B= Backup	FB= Field Blank
* = Split	S= Spike	BG= Background	BM= Blank Matrix
A= Acidified	U= Unacidified	RB= Rinse Blank	

STORAGE LOCATION CODES refer to the storage location of each sample and the storage facility.

F= Fresno	R= Refrigerator	SR10= Sacramento Refrigerator #10
S= Sacramento	F= Freezer	SF05= Sacramento Freezer #05
W= Warehouse	A= Air Temp	SF06= Sacramento Freezer #06
L= Lab	I=Ice Chest	SF07= Sacramento freezer #07
D= Deep Freeze	FZ= Freezesafe	

SAMPLE TYPE CODES refer to the sample matrix collected.

FRU= Fruit	DVEG= Dislodgeable Vegetation	TWG= Twigs
SOI= Soil	SSS= Stainless Steel Sheets	EXT= Extract
WAT= Water	STD= Standard	VEG= Vegetation
SUR= Surrogate	SED= Sediment	FILT= Filtrate
TUR= Turf	TAN= Tank	KIM= Kimbie
SAN= Sand	AIR= Air	TRP= Air Cassettes
BRA= Branch		

SAMPLE CONTAINER CODES refer to the type of container each sample is placed in during storage.

QMSJ= Quart Mason Jar	1LAMBR= 1 Liter Amber Bottle
PMSJ= Pint Mason Jar	HPMSJR= Half Pint Mason Jar
PBAG= Plastic Bag	HIVJAR= Hi-Vol Jar
FOIL= Aluminum Sheets	P500mL= Plastic Bottle (500 mL)
CAS= Air Cassettes	1LPC= 1 Liter Polycarb. Bottle

1LPP= 1 Liter Polyprop. Container
XADT= XAD Tube (small)
Summa= Summa Canister
HIV= High Volume Air Sampler_
500mLPC= 500mL Polycarb. Container
250mLAMBR= 250mL Amber Bottle
500mLAMBR= 500mL Amber Bottle
500mLHDPP= 500mL High Density Polyprop.
VIAL= Small Standard Vial
XAD4= Large XAD 4 Tube
LOV= Low Volume Air Sampler

LABORATORY CODES refer to the specific laboratory each sample is shipped to for analysis.

QUAN= Quanterra Laboratory
ATL= Aquatic Toxicology Lab
FMC= FMC Corporation
ZEN= Zeneca Ag Products
APPL= Apple Labs
NCL= North Coast Labs
FRES= Fresno Soils Lab
CDFA= CA Dept. of Food & Agr.
CDFG= CA Dept. of Fish & Game
ALTA= ALTA Analytical Laboratory
VAL= Valent Dublin Laboratory
MOR= Mores Laboratories Inc.
UCD= University California Davis
WSAC= W. Sacramento Soils Lab

ANALYSIS TYPE refers to the type of test method to be performed on each sample.

C= Chemical
O= Organic
T= Texture
F= Tracer
P= pH
B= Bulk Density
E= Elisa
M= Moisture
V= Various

CHEMICAL ANALYSIS refers to the chemical analysis to be performed on each sample, if applicable.

OP=Organophosphate Screen
CB= Carbamate Screen
DI= Diazinon
EN/DI= Endosulfan/ Diazinon Screen
TOX= Biotoxicity
HEX=Hexazinone
TRI= Triclopyr
GLY= Glyphosate
TRIAZ= Triazine Screen

TDM= Triclopyr, 2,4-D, MCPA
PIC= Chloropicrin
MOL= Molinate
CARBO= Carbofuran
MeBr= Methyl Bromide
PROP= Propanil
THIO= Thiobencarb
MP/MN= Methyl Parathion/Malathion

COMMENTS refers to any additional information regarding samples.

BS= Blind Spike
ACT TOX= Acute Tox
CHN TOX= Chronic Tox
RB= Rinse Blank
GF= Golden Fleece
BB=Buck Brush
BF= Bracken Fern
MB= Manzanita Berry
SR= Soap Root
DB= Deer Brush
EB= Elderberry
DG= Deergrass
RD= Redbud
PE= Pearly Everlasting

2.2 Sample Check-in Procedures

All samples received at the storage facility are immediately put in a refrigerator or freezer depending on the matrix specific storage requirements. The field crew fills out a three part check-in sheet (Figure A) using the sample tracking codes (Section 2.1).

The check-in sheet must be complete in order to properly track environmental samples. The following is a description of each key component of the check-in sheet.

Portion Filled Out By Field Staff

Project ID: The study number or name.
Date Received: The date the sample was received from the field crew.
Checked-in by: The initials of the person who fills out the check-in sheet.
Remarks: List ice chest number where samples were stored, Hobo Temp® temperature logger number (if necessary), and any additional or necessary information regarding the samples listed on the check-in sheet. For GLP studies, the ice chest number along with the maximum temperature samples were stored at in the ice chest must be marked on Hobo Temp® print-out as noted in SOP EQOT001.01. If temperature exceeded 6° C for refrigerated samples or 0° C for frozen samples, this must be documented on the sample check-in sheet in the comments section.
EHAP Sample No.: The number assigned to a labeled sample container.
Sample Code: List sample code (Section 2.1 for codes).

Date Sample Collected: Note the sample collection date from the Chain-of-Custody.
Sample Type: Specify the type of sample collected (Section 2.1).
Container Type: What the sample is stored in (Section 2.1).
Analysis Type: The type of analysis the sample is intended for (Section 2.1).
Analysis: List the type of chemical or screen the sample is to be analyzed for.
Comment: Space provided for additional information regarding individual samples (Section 2.1).

Portion Filled Out By Sample Custodian

Date/Logged in by: The date and person who enters information into the Sample Tracking Database.
Storage Location: List where the sample is being stored (Section 2.1).

After the check-in sheet is completed, the white and yellow copy are used to enter the information into the Sample Tracking Database and then filed with the QA/QC officer. The pink copy is given to the project leader in order to track ice chests and corresponding samples entering the storage facility (GLP studies only).

Each field sample is compared against it's corresponding Chain-of-custody (COC), then the COC is signed and dated by the person receiving the sample at the storage facility. The white and yellow copy of each COC is removed and sent with it's corresponding field sample to the laboratory. The pink COC copy is given to the Project Leader. Any remaining samples held at the storage facility are stored under their required storage conditions with the white and yellow copy of their corresponding COC's.

2.3 Sample Check-out Procedures

A three part check-out sheet is filled out for any sample leaving the storage facility (Figure B). The check-out sheet must be complete in order to properly track environmental samples leaving the storage facility. The check-out sheet is filled out by the sample custodian only.

The check-out sheet is similar to the check-in sheet but differs in three components.

> **Date Delivered:** The date the sample is taken to the laboratory.
> **Checked-out by:** The initials of the person filling out and transporting the sample to the laboratory.
> **Laboratory Delivering to:** Specify the destination code for the sample scheduled for analysis (Section 2.1).

A pink copy of the check-out sheet and the white and yellow copies of each COC are placed in a plastic bag and accompany samples transported to the laboratory. The samples are placed in ice chests and maintained at their required temperatures during transport using blue ice, wet ice or dry ice. The white and yellow copies of the check-out sheet are retained by the QA/QC officer and are used to enter information into the Sample Tracking Database.

2.4 Chemistry Results

After results are received from the laboratory, the laboratory sample number, and the extraction and analysis date for each sample are entered into the Sample Tracking Database using the appropriate Microsoft Access query.

2.5 Sample Disposal

After each study is completed, and with the approval of the Project Leader, all remaining samples stored in the storage facility may be disposed of by the sample custodian. A two part Sample Disposal Sheet is completed and includes information similar to the check-out sheet (Figure C). This information is then entered into the Sample Tracking Database using the appropriate Microsoft Access query. The white copy of the Sample Disposal Sheet is retained by the QA/QC officer while the yellow copy is used to enter the information into the database.

3.0 Sample Tracking Database

All the information reported on the check-in, check-out, and sample disposal sheets is entered in the Sample Tracking Database using tables in Microsoft Access. Queries, forms and reports are designed specifically for each study to access fields for summarizing data.

3.1 Computer Generated Backups

Weekly backups are conducted by copying the database to a zip drive disk.

FIGURE B

STATE OF CALIFORNIA

SAMPLE **CHECK-OUT** SHEET

DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
West Sacramento Field Office
3971 Commerce Drive, Suite D
West Sacramento, CA 95691 (916) 322-3082

Study Number (Project ID):_____ Logged Out By (data entry):_____

Date Delivered:_____ Data Entry Date:_____

Checked-Out By:_____ Storage Location Code:_____

Laboratory Delivering To:_____ Page ____ of ____

Remarks:

EHAP Sample #	Sample Code	Date Sample Collected	Sample Type	Container Type	Analysis Type	Analysis	Comments

(5/98) White copy-Lab Liaison, Yellow-Sample Tracking Staff, Pink-Laboratory

FIGURE A

SAMPLE CHECK-IN SHEET ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

Study Number (Project ID):_____

Date Received (Warehouse):_____

Checked-In By:_____

Page ____ of ____

Sample Tracking Staff Only:

Logged In By (data entry):_____

Data Entry Date:_____

Storage Location Code:_____

Remarks:

Samples were stored in ice chest # _____ at check-in.

EHAP Sample #	Sample Code	Date Sample Collected	Sample Type	Container Type	Analysis Type	Analysis	Comments

(3/99) White copy-Lab Liaison, Yellow-Sample Tracking Staff, Pink-Project leader

FIGURE C

California Dept. of Pesticide Regulation
Environmental Hazards Assessment Program
3971 Commerce Drive, Suite D
West Sacramento, CA 95691
(916) 322-3082

Today's Date:_____

Sample Disposal Sheet

Project ID (Study no.): _____ Disposed by: _____

Date Disposed: _____ Storage location: _____

==========

Remarks:

==========

EHAP Sample #	Sample Code	EHAP Sample #	Sample Code	EHAP Sample #	Sample Code	EHAP Sample #	Sample Code

SUPPLEMENT 9
EHAP Standard Operating Procedure ADMN005.00
Archiving Study Data, Records, and Other Documents

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
1020 N Street
Sacramento, California 95814

STANDARD OPERATING PROCEDURE
Archiving Study Data, Records, and Other Documents

KEY WORDS

archivist; quality assurance; SOP; project leader; check-in; check-out; GLP

APPROVALS

APPROVED BY: John D. Sanders DATE: 3/6/97
Management

APPROVED BY: [signature] DATE: 2-25-97
EHAP Senior Scientist

APPROVED BY: Randy Segawa DATE: 2-26-97
EHAP Quality Assurance Officer

PREPARED BY: [signature] DATE: 2-24-97

Environmental Hazards Assessment Program (EHAP) organization and personnel such as *management, senior scientist, quality assurance officer, project leader, etc.* are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE
Archiving Study Data, Records, and Other Documents

1.0 INTRODUCTION

1.1 Purpose

This Standard Operating Procedure (SOP) describes the archiving procedures for all records and data associated with studies conducted by the Environmental Hazards Assessment Program (EHAP), Department of Pesticide Regulation, California Environmental Protection Agency. This SOP should be followed for the archiving of all study data.

1.2 Definitions

Archivist is the individual responsible for maintaining the archives.

Project leader is the individual responsible for the overall conduct of a study.

Study file is the file containing all of the records and data for a study.

Study number is the unique identification number assigned to each study.

2.0 MATERIALS

none

3.0 PROCEDURES

3.1 Archived study files shall consist of all raw data, field notes, protocols, interim reports, and a master copy of the final report. Correspondence and other documents relating to interpretation and evaluation of data must also be included in the study file if they are not included in the final report. Raw data results will in most cases consist of the original chain of custody with the analytical result and chemist signature (white copy).

3.2 Study files will be retained by the project leader until the final report is approved. At that point, the project leader will give the study file to the archivist. During the period between initiation of the study and final report approval, the archivist will include the location of the study file in the archives index.

3.3 Archiving of study files must be done only by the archivist. The project leader must organize the study file so that information is readily retrievable from within the file.

3.4 The project leader shall provide the archivist with an electronic copy of the final report. For studies conducted under Good Laboratory Practices, additional requirements will apply (U.S. EPA, 1992), including the following:

3.4.1 Photocopied material shall not be included in the study file.

3.4.2 All field notes, data records, etc. must be in ink.

3.5 The archivist shall be the only individual with access to the archives. The archivist will designate an alternate when he/she is absent.

3.6 The study files shall be filed numerically by study number. The project leader must request a study number prior to the beginning of the study. Each protocol must have **a** study number for approval.

3.7 An index of the archived study files shall be kept by the archivist. Other individuals may have copies of this index upon request.

3.7.1 The index shall list the study files numerically by study number.

3.7.2 Each entry on the index shall list the study number, the date the study file was archived, and the title of the study.

3.7.3 The index shall list the location of files for studies still in progress, as stated in section 3.2

3.8 Requests for information contained in archived files will be made to the archivist. Check-in/out procedures are as follows:

3.8.1 Archivist retrieves study file.

3.8.2 The study file number is recorded on the check-in/out log. The check-out date will be recorded, and the archivist and requestor will initial it.

3.8.3 No alterations or additions shall be made to the files while in the borrower's

possession.

3.8.4 The study file shall be returned to the archivist by the same individual who checked it out. The file shall be returned in the same organized manner as it was checked out. The check-in date will be recorded in the log and the archivist and the borrower shall initial it.

3.8.5 The archivist is responsible for refiling the study file in the archives.

3.9 A check-in/check-out log will be kept by the archivist. This log shall contain the following information:

3.9.1 The study number.

3.9.2 The name of the borrower.

3.9.3 The check-out date.

3.9.4 The check-in date.

3.9.5 Spaces for the archivist and borrower to initial both the check-in and check-out dates.

3.10 Electronic copies of final reports will be stored indefinitely in a manner that prevents deterioration and insures that copies are easily accessible by the archivist. It is the responsibility of the archivist to manage these files, updating electronic format when appropriate. When updates are necessary, the archivist will state the type of change on the archive index, initial, and date the entry.

3.11 Study files will be retained for a minimum of five years. After that time, the archivist may continue storage of files, or transfer to another location. In all cases, study file transfers or disposals will be noted in the archives index.

4.0 REFERENCES

U.S. Environmental Protection Agency. 1989. Federal Insecticide Fungicide, and Rodenticide Act (FIFRA); Good Laboratory Practice Standards; Final Rule.

U.S. Environmental Protection Agency. 1992. Federal Insecticide Fungicide, and Rodenticide Act (FIFRA) Good Laboratory Practice Standards (GLPS) Questions and Answers. Office of Prevention, Pesticides, and Toxic Substances.